SOLUTIONS

PRINTED BY
SPOTTISWOODE AND CO., NEW-STREET SQUARE
LONDON

SOLUTIONS

BY

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BEING THE FOURTH BOOK, WITH SOME ADDITIONS, OF THE SECOND EDITION OF OSTWALD'S 'LEHRBUCH DER ALLGEMEINEN CHEMIE'

TRANSLATED BY

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LONDON

LONGMANS, GREEN, AND CO.

AND NEW YORK: 15 EAST 16th STREET

1891

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TRANSLATOR'S NOTICE

The advances made in the study of the difficult subject of Solutions in the last three or four years have been both rapid and astonishing. A new theory has been started, and has grown to maturity in a very short time. This theory professes to account not only for the main facts concerning solutions, but also for a host of other facts besides.

The facts amassed about solutions are now so many, and the theory is now so fully developed, that a systematic arrangement of these facts, and an authoritative statement of the theory, are sure to be welcomed by all chemists. Such a setting forth of facts and theory is to be found only in one book, and that is Professor Ostwald's *Lehrbuch der Allgemeinen Chemie*, the second edition of which appeared in the end of last year. This book is certainly *the* text-book of general chemistry.

It was with the greatest pleasure that I agreed to prepare a translation of those chapters of the *Lehrbuch* which deal with the subject of solutions. Professor Ostwald has kindly allowed use to be made of chapters and portions of chapters in other parts of the *Lehrbuch*, so as to insure that the whole subject shall be set fairly before the English reader; for the same purpose he has also modified and added to the text here and there.

The translation, I think, expresses the sense of the original.

I hope this book will be serviceable in showing clearly what is known in the department of natural science with which it deals, and that it will incite to the more full investigation of the varied phenomena of solutions.

M. M. PATTISON MUIR.

CAMBRIDGE: *June* 1891.

PREFACE

THIS book is a translation of that portion of my *Lehrbuch der Allgemeinen Chemie* which deals with the Laws of Solutions.

There are always objections to publishing a portion of a book; but in the present case, the issue of a part of a larger book seems to be justified by the consideration that a comprehensive survey of the very remarkable advances, both theoretical and practical, which have been made in the last few years in the subject of solutions must be useful to all who are not in a position to make themselves acquainted with the many and widely-scattered memoirs on this subject. The great rapidity with which the theory of solutions, founded by van 't Hoff, has advanced in recent years is perhaps the reason why doubt has been cast on the solidity of this theory; for the more rapid is the advance of new ideas the more difficult is it for those who stand on one side to criticise these ideas. The author hopes that the statement of this theory which he lays before the scientific public, with its debit and credit sides duly made up, will enable them to arrive at just conclusions concerning its value.

It is not to be denied that there are still several points in the theory in question which require explanation; but this is true of all theories, even of those which are most firmly established. The very many applications which

have been made of the theory, and the very various departments of investigation which have been elucidated by it, show that it already fulfils the essential conditions of a good theory, inasmuch as it serves as a guide to advance while at the same time it helps in setting forth the knowledge already gained; and these considerations lead us to expect that the theory will do yet more in the future than it has done in the past.

In order to make this book as useful as possible in this direction, and at the same time to give it as far as may be an individual character, the author has revised the text and has made changes and improvements where these seemed called for. Additions have also been made from memoirs which have appeared since the publication of the German edition at the end of the year 1890.

My best thanks are due to Mr. Pattison Muir for the care with which he has prepared the translation into English.

Finally, the author has revised the proofs of the English edition in order to insure the accuracy of the translation.

W. OSTWALD.

Leipzig: *June* 1891.

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ERRATA AND ADDENDA

P. 8, line 16 from top, *for* 'law' *read* 'laws'

,, 13, ,, 7 ,, *insert* bracket after t in the formula.

,, 20, figure should be numbered '2.'

,, 32, lines 11 and 12 from bottom, *for* 'becomes' *read* 'became'

,, 44, line 18 from top, *after* p_1 d_1 *insert* :

,, 45, ,, 5 ,, *after* $\frac{q_1}{p_1}$ *insert* :

,, 45, lines 14, 15, and 18 from top, *for* 'vapour-pressure' *read* 'vapour-pressures'

P. 67, line 5 from bottom, *for* 'Etard' *read* 'Étard'

,, 68, ,, 6 from top, *for* 'equation' *read* 'equations'

,, 78, ,, 8 ,, move sign of equality a little lower.

,, 99, at end of quotation from Pfeffer's memoir add reference as follows:—'A paper is published in *Chem. Soc. Journal*, June 1891 (TRANS. 1891, p. 344) by R. H. Adie, in which a full account is given of the preparation of membranes in clay-cells.'

P. 104, to first foot-note add, 'Quite recently R. H. Adie has carried out a series of measurements of the osmotic pressures of many salts in solution (*Chem. Soc. Journal*, TRANS. 1891, p. 344).'

P. 136, line 13 of table, *for* 'ammonium' *read* 'ammonia'

,, 142, ,, 18 from top, and also last line, *for* '$r' : r$' *read* '$r : r'$'

,, 160, first table, column 1, *for* '660, 100, 1980' *read* '60·9, 81·0, 100·6.'

,, 165, line 4 from bottom, *for* 'solution' *read* 'solutions'

,, 237, ,, 2 ,, reverse the second bracket in the formula.

,, 256, ,, 2 from top, *for* '$(1-a)$' *read* '$(1-b)$'

,, 256, ,, 3 ,, *for* 'a' *read* 'b'

,, 297, ,, 20 ,, *for* 'the actual molecular weights of' *read* 'the molecular weights found for'

P. 302, line 7 from top (not counting table) *for* 'regulations' *read* 'regularities'

P. 304, line 2 from top, *for* 'was' *read* 'is'

ADDITIONAL ERRATA AND EMENDATIONS.

P. 17, line 13, *let the sentence read*: 'The composition of the mixture was calculated from the observations of the gases absorbed . . .'

P. 22, lines 7 and 9, *for* 'leaving' *read* 'striking'

„ 30, line 10, *the equation should read thus*: $y = a\, e^{-\frac{k}{x}}$

„ 41, lines 18 and 19 from bottom, *should read*: 'when placed under boiling water it combines with the water, and in so doing becomes liquid;'

P. 41, line 4 from bottom, *delete* '100 parts of'

„ 42, lines 8 and 9, *should read*: 'The two parts of the curve may be placed unsymmetrically;'

P. 57, line 4, *delete* 'internal'

„ 57, „ 9, *for* 'internal pressure' *read* 'pressure towards the interior'

„ 71, lines 7 and 8, *should read*: 'i.e. more heat is taken up in solution, or, as the case may be, more is evolved, as temperature rises.'

P. 72, line 13, *for* $\frac{\rho\, d\, \mathrm{T}}{d\, \mathrm{T}^2}$ *read* $\frac{\rho\, d\, \mathrm{T}}{\mathrm{R}\, \mathrm{T}^2}$

„ 73, „ 8 from bottom, *for* $\int \frac{\rho}{\mathrm{R}\, \mathrm{T}^2}$ *read* $\int \frac{\rho\, d\, \mathrm{T}}{\mathrm{R}\, \mathrm{T}^2}$

„ 125, lines 1 and 2, *for* 'surrounded' *read* 'included'

„ 125, line 7, *for* $\sum \frac{(-1)_p}{2p+1}$ *read* $\sum \frac{(-1)^p}{2p+1}$

„ 125, „ 14, *between* 'which' *and* 'quickly' *insert* 'nevertheless'

„ 125, lines 17 and 18, *should read*: 'the third term, and all the following terms . . .'

P. 125, line 20, *for* 'closed' *read* 'finite'

„ 125, „ 7 from bottom, *for* 'time t' *read* 'time $2t$'

„ 126, „ 19, *for* 'aside' *read* 'out of its course'

„ 127, „ 24, *let the equation be*: $\mathrm{E} = \mathrm{A} e^{-\frac{\pi^2}{\mathrm{H}^2} k' t}$

„ 136, „ 16, *for* 'square root' *read* 'square'

„ 136, „ 13 of table, *for* 'Ammonium' *read* 'Ammonia'

„ 145, „ 15, *for* 'in this portion' *read* 'at this place'

„ 145, „ 15, *for* 'pressure of the quantity' *read* 'pressure on the quantity'

P. 147, „ 3, *for* '1 centim.,' *read* '·1 centim.,'

„ 166, lines 3–6, *let the sentence read*: 'If the air is saturated with water-vapour, then, as condensation is made easier by the pressure of dust-particles, the smallest expansion, and consequent lowering of temperature, suffice to produce a cloudiness'

Pp. 186 and 187, lines 5 from bottom and 7 from top, *for* $l\frac{b}{f}$ *read* $l\frac{f}{f'}$

P. 218, lines 13 and 12 from bottom, *should read*: 'the numbers in the second column by the molecular weights of the salts'

P. 218, line 8 from bottom, *for* 'atomic' *read* 'molecular'

„ 219, bottom line, and line 5 from bottom, *replace* 't' *in equation by* 'T'

P. 237, line 6 from bottom, *for* $\frac{1}{b}$ *read* $\frac{1}{v}$

„ 238, „ 7, in equation, *for* $\frac{b-B}{1-C}$ *substitute* $\frac{b-BC}{1-c}$

„ 247, lines 4 and 3 from bottom, *delete* 'no mutual . . . ions occurs,' *and substitute*: 'the properties of the ions are not affected by their mutual actions'

P. 248, lines 14 to 18, *delete sentence, and substitute*: 'Chemical compounds have for the most part an individuality of behaviour which forbids conclusions to be drawn from analogy, except in the cases of very closely allied substances, and even in such cases the correspondence in behaviour is not always regular.'

P. 294, line 17, *for* 'each' *read* 'the former'

„ 295, „ 2, *for* '10·48' *read* '10·84'

„ „ „ 8 from bottom, *before* 'proportional' *insert* 'inversely'

„ 296, „ 12, *transpose the words* 'ether' *and* 'water'

„ 301, „ 9, *for* 'the same quantity' *read* 'a constant proportion'

„ 302, „ 13 from bottom, *for* 'quantities' *read* 'percentages'

„ 303, „ 3 after table, *for* 'quantities' *read* 'percentages'

SOLUTIONS

CHAPTER I

SOLUTIONS IN GASES

1. Generalities.—Solutions are homogeneous mixtures which cannot be separated into their constituent parts by mechanical means. The ability of substances to form such mixtures or solutions varies according to the states of aggregation of the substances. In the case of gases the ability is universal and unlimited; two gases can always form homogeneous mixtures with one another in all proportions, provided they do not combine together chemically. The conditions under which liquids and solids form solutions with one another are much more restricted. Liquids, it is true, generally dissolve one in another, but the number of pairs of liquids which mutually dissolve in all proportions is not great. Solids scarcely dissolve in solids; although isolated facts have long been known, it is only recently that the conception of solid solutions has been clearly established.[1]

2. Solutions of gases in gases.—The properties of a homogeneous mixture, or solution, formed by two gases are the sum of the properties of the constituents of the mixture. This statement holds good for all gaseous solutions, and enables us to draw conclusions regarding properties which have not yet been subjected to experimental examination.

[1] Van 't Hoff, *Zeitschr. f. physikal. Chemie*, **5**, p. 322 [1890].

The limits within which this statement holds good are much the same as those which condition the general gaseous laws. As the statement does not hold good for liquids, gases show deviations from it the nearer they are brought to the liquid condition.

The earliest known special case of the foregoing general statement was that which applies to the pressure of gaseous mixtures. Dalton (*Gilb. Ann.* **12**, p. 385) announced in 1802 that the total pressure of a mixture of gases is the sum of the partial pressures exerted by the constituents of the mixture in the given space. This simple and perfectly correct statement has often been misunderstood. From certain expressions used by Dalton, the conclusion has been drawn that 'the different gases exert no pressure on one another;' and then this conclusion has been regarded as disproved by the fact that two differently coloured gases, placed one over the other, suffer simultaneous and proportional change of volume when the pressure is changed, and therefore 'exert pressure on one another.' Two different cases are really under consideration. When two, or more than two, gases are in contact, the following equation holds good

$$p_1v_1 + p_2v_2 + p_3v_3 + \ldots = \text{P V};$$

where $p_1 p_2 \ldots$ and $v_1 v_2 \ldots$ are the pressures and volumes of the constituent gases, and P and V are the corresponding values for the mixture of gases. If the gases are superimposed in layers, all the pressures must be equal; the equation takes the form

$$p(v_1 + v_2 + v_3 + \ldots) = \text{P V}, \text{ or } v_1 + v_2 + v_3 + \ldots = \text{V};$$

in this case the volume of the mixed gases is equal to the sum of the volumes of the individual gases. But if the gases are equally mixed, all the volumes are equal, and therefore

$$\text{V}\,(p_1 + p_2 + p_3 \ldots) = \text{P V}, \text{ or } p_1 + p_2 + p_3 \ldots = \text{P};$$

in this case the pressure of the mixed gases is equal to the

sum of the pressures of the individual gases. The second case is the more common; it occurs when a mixture of gases, made in any order, is allowed to remain at rest for a time.

It is not only the pressure and volume of a mixture of gases which are equal to the sum of the individual pressures or volumes; the statement has been proved true for refraction of light,[1] and also for absorption of light.[2] There can be little doubt that the generalisation will apply in all other cases.

3. **Deviations.**—The cause of the gaseous laws, in their simplest form, in which they are independent of the nature of this or that special gas, is to be found in the great division of the particles of the gases throughout a considerable space; under such conditions the characteristic properties of the particles do not come into play, and these particles act only by their number. The same cause lies at the root of the *law of addition* of gaseous properties, stated in the preceding paragraph. Deviations from this law, as from the general gaseous laws, are to be looked for if the conditions already expressed differ more from reality than is allowed by the necessary experimental errors.

But little is known concerning such deviations. Regnault[3] determined the volume, at different pressures, of mixtures of air with carbon dioxide and of hydrogen with sulphur dioxide; he noticed deviations from the results calculated from the behaviours of the individual gases, but the relations could not be formulated simply. The researches of Andrews[4] on mixtures of air and carbon dioxide, and on mixtures of nitrogen and carbon dioxide,[5] go more deeply into the matter, and show that the simple law of addition requires modification. Calculations have been made, from the results of Andrews, by Margules[6] and

[1] Biot and Arago; *Gilb. Ann.* **25**, p. 345 [1807].
[2] Bunsen and Roscoe; *Pogg.* **101**, p. 248 [1857].
[3] *Mém. de l'Acad.* **26**, p. 256. [4] *Phil. Mag.* (5) 1, p. 78 [1876].
[5] *Phil. Trans.* 1887, p. 45 (published after Andrews' death).
[6] *Wien. Akad. Ber.* **97**, p. 1399 [1888].

Galitzine.[1] The calculations of Margules show that a notable expansion occurs when strongly compressed carbon dioxide and nitrogen are mixed; this expansion had been noticed by Andrews. For instance, the following increase of volume was noticed when three volumes nitrogen were mixed with four volumes carbon dioxide at 31·1°:—

Pressure	50	60	70	80 atmospheres
Expansion	9	12	29	39 per cent.

On the other hand, no marked difference was found between the total pressure and the sum of the partial pressures; thus

Total pressure (at 31·1°) .	50	60	70	80 atmospheres
Sum of the partial pressures	50·7	61	71·4	81·6 atmospheres.

The results of the calculations of Galitzine are similar to these.[2] He found the sum of the partial pressures, at low temperatures, to be a little greater than the observed total pressure; the deviation acquired a maximum value as pressure increased; after passing the maximum, the value decreased until it disappeared at 150 atmospheres, temperature being 31°; at greater pressures than this the deviation changed its sign, so that at the highest pressures the total pressure was greater than the sum of the partial pressures. The deviations were found to be very small at temperatures above the critical temperature.

F. Braun[3] has carried out investigations with various gases. The gases were placed in two vessels, v_1 and v_2, connected by stopcocks: the vessels were in connexion with a manometer, the other limb of which, for obtaining a constant pressure, was connected with another vessel having a capacity equal to $v_1 + v_2$; on opening the stopcock the gases mixed, and the manometer showed the change of pressure. This change of pressure consisted of the change accompanying the expansion of the gases to double their volume, and the change consequent upon the

[1] *Dissertation*; Strassburg, 1890. [2] *Loc. cit.* p. 23 *et seq.*
[3] *Wied. Ann.* **34**, p. 943 [1888].

mutual reaction of the two gases. The first value could be calculated from the known behaviour of the gases, and from this the second value was found. The second values are given in the following table in mm. of mercury, calculated at 0° and an initial pressure of one atmosphere.

Gases	Regnault	Fuchs
$SO_2 + CO_2$	−5·28 mm.	−3·88 mm.
$SO_2 + H_2$	−1·36 mm.	−0·16
$SO_2 + N_2$	−2·67	−1·27
CO_2 + air	−0·36	
$CO_2 + H_2$	+0·04	
H_2 + air	+0·22	
$H_2 + N_2$	+0·43	

The *minus* sign signifies a decrease of pressure. The numbers in the two columns are obtained by using observations of Regnault and of Fuchs on the behaviour of sulphur dioxide at various pressures. It is evident that both increases and decreases of pressure occur.

4. **Solutions of liquids in gases.**—The readiness shown by liquids to form homogeneous gaseous mixtures with gases is connected with the readiness of these liquids to evaporate—in other words, to assume the gaseous state. Dalton[1] expressed the law, which corresponds with the *law of addition* for solutions of gases:—*the vapour-pressure of a liquid in a gas is the same as in a vacuum.*

This law must be regarded as a limiting law. The laborious measurements of Regnault[2] on the vapour-pressure of ether in air show that this pressure has nearly the same value as in an empty space, but that in air the pressure is regularly a little less than *in vacuo*; the difference may somewhat exceed 5 per cent. of the pressure. Deviations were also observed with carbon disulphide and benzene in air, but the differences were much smaller than with ether in air.

[1] *Gilb. Ann.* **12**, p. 393 [1802]; **15**, p. 21 [1803], from *Mem. Manchester Phil. Soc.* **5**, p. 550.

[2] *Mém. de l'Acad.* **26**, p. 679.

It was difficult, if not impossible, to observe quite constant pressures in these measurements; irregularities were frequently observed, and were attributed by Regnault to the condensing action of the walls of the containing vessel. The experiments of Guglielmo and Musina[1] have shown that Regnault's explanation is not tenable, or at least is not sufficient. It is much more likely that the ether which Regnault used contained traces of impurities which caused partial condensation. Recent measurements of Tamman[2] and Beckmann[3] have shown how difficult it is to obtain ether with a constant vapour-pressure.

Galitzine[4] has recently published an extensive investigation into the subject now under consideration; a part of the foregoing historical summary is taken from this memoir. It is shown that the differences between the vapour-pressures of water, ether, and ethylic chloride, in air, and *in vacuo*, are very small; these differences increase at high temperatures, but, as a rule, do not amount to 1 per cent. The differences become considerably greater; they are, however, irregular, when the experiments are conducted in narrow tube-shaped vessels. The cause is to be sought for in the slow diffusion, and consequent coming into play of the action of the walls of the vessel.

Two causes are to be regarded as operative in the phenomena we are considering: the mutual actions between the molecules of the vapour and the gas must be considered; and the lowering of the vapour-pressure of the liquid, due to the solution in the liquid of some of the gas, must not be overlooked. In the case of such a gas as air, which dissolves very slightly in liquids, the second cause cannot exert much influence; but this cause becomes operative when a gas of greater solubility, such as carbon dioxide, is used. Observations of such cases were made by Regnault;

[1] *Riv. Scient. Firenze*, **19**, p. 185 [1887].
[2] *Wied. Ann.* **32**, p. 683 [1887].
[3] *Zeitschr. f. physikal. Chemie*, **4**, p. 536 [1889].
[4] *Dissertation*; Strassburg, 1890.

these have been referred to already. No more recent investigation is known to me.

A theory of the behaviour of mixed gases has been given by van der Waals;[1] it is based on the general theory of gases put forward by the same author.[2] Certain changes are made in the equation for a single gas, $pv = RT$; where R is a constant, and T = absolute temperature. In the first place, Boyle's law is not applied to the total space, but only to that part which is not occupied by the molecules of the substance; the volume of the molecules, b, is subtracted from the total volume, v. Further, the pressure consists not only of the kinetic portion, which is referred by the theory to the bombardment of the molecules, but also of a portion which is dependent on the mutual actions of the molecules, and which is proportional, according to van der Waals, to the square of the density, or is inversely proportional to the square of the volume. The equation given above then assumes the form $\left(p + \frac{a}{v^2}\right)(v - b) = RT$, where a = the constant of the mutual molecular actions. That this equation expresses the behaviour of gases in changing to the liquid state, has been shown by van der Waals in the memoir referred to. The equation may be written $p = \frac{RT}{v - b} - \frac{a}{v^2}$.

In dealing with mixed gases, a corresponding equation is used, in which the constants a and b are replaced by functions of the constants, a_1 b_1, and a_2 b_2, belonging to both parts of the mixture. In a twofold mixture, consisting of the parts $1 - x$, and x, a is replaced by $a_x = a_1 (1 - x)^2 + 2 a_{12} x (1 - x) + a_2 x^2$, where a_1 and a_2 are the constants of the molecular attraction of the single substances, and a_{12} is the corresponding constant for the reaction of the different molecules. The constant b cannot be replaced by the expression $b_x = b_1 (1 - x) + b_2 x$, but,

[1] *Zeitschr. f. physikal. Chemie*, 5, p. 133 [1890].

[2] *Die Continuität des gasformigen und flüssigen Zustandes*: Leipzig, 1881.

according to Lorenz,[1] the expression to be used is $b_x = b_1 (1 - x)^2 + b_{12} x (1 - x) b_2 x^2$, where b_{12} is a new constant.

The further development of the theory leads to somewhat complicated calculations. Van der Waals has shown that the theory enables several phenomena to be represented qualitatively; but the measurements hitherto made do not lead to such an exact quantitative knowledge as is required for the accurate determination of the new constants. Galitzine[2] has put forward a theory similar in principle to that of van der Waals. This theory is founded on the equation given by Clausius.[3]

5. **Solutions of solids in gases.**—Inasmuch as certain solids can be evaporated without going through the liquid condition, it is correct to speak of the solution of such solids in gases. We have no experimentally-gained acquaintance with the law of these phenomena; nevertheless, considering that the vapour-pressure of volatile solids is a function only of the temperature, as is the case also with liquids, we may conclude that Dalton's law will hold good for solutions of solids in gases. Because of the circumstance that gases do not dissolve, or dissolve only to a very slight degree, in solids, the deviations from Dalton's law which are noticed for some liquids will not occur for solutions of solids in gases.

The specific mutual action between the molecules of the solvent and those of the dissolved substance appears sometimes to act so that the volatility of the dissolved substance is increased. Hannay and Hogarth[4] found that gaseous alcohol, above its critical temperature, dissolves potassium iodide; this salt had therefore becomes gaseous at a temperature whereat it ordinarily shows no marked volatility. It is certain that actions of this kind can take place only in gases which assume a small volume at very great pressure, as otherwise the mutual action of the molecules cannot attain a considerable value.

[1] *Wied. Ann.* **12**, p. 134 [1881]. [2] *Loc. cit.*
[3] *Wied. Ann.* **9**, p. 348 [1880]. [4] *Proc. R. S.* **30**, pp. 178, 484 [1880].

CHAPTER II

SOLUTIONS OF GASES IN LIQUIDS

1. The fundamental law.—It may be asserted that every liquid is capable of taking up every gas, and combining therewith to form a homogeneous liquid or solution. This capability, however, differs very much, and is dependent, in complicated ways, on the nature of both the substances.

Two classes of these gas-solutions are to be distinguished. To the first class, the ordinary solutions, belong those from which the dissolved gas is entirely removed by raising temperature or diminishing pressure; to the second class belong those from which the dissolved gas is not thus entirely removed. In cases belonging to the second class, e.g. in a solution of hydrogen chloride in water, we have sufficient grounds to assert that chemical change occurs.

The law of Henry,[1] verified by Bunsen,[2] holds good for solutions from which the dissolved gas is wholly removed by lowering pressure or raising temperature: *the quantity of a gas dissolved by a specified quantity of a liquid is proportional to the pressure of the gas.* As the volume of a gas is inversely proportional to the pressure, the law may be put thus: *a specified quantity of a liquid dissolves the same volume of a gas at all pressures.* There is no question about the proportions of gas and liquid so long as the quantity of gas is not smaller than that which can be absorbed by the liquid under the experimental conditions.

[1] *Phil. Trans.* 1803. [2] *Annalen*, 93, p. 1 [1855].

This cannot occur when the gas and liquid together occupy a space which is kept constant; for in this case the gaseous pressure falls, when absorption occurs, until the quantity of gas which corresponds to the decreased pressure is absorbed.

Another form is obtained for Henry's law by bringing in the notion of *concentration*. Taking concentration to mean the quantity of substance divided by the space which it occupies (whether other substances be also present in this space or not), the law may be expressed by saying that *the gas is absorbed by the dissolving liquid in such quantity that the concentration of the gas in the space occupied by it is proportional to that in the liquid*. The absolute value of the concentration has no effect on the proportion of the two concentrations; this depends only on the nature of the substances, and on the temperature.

2. **Gas-mixtures.**—In 1807 Dalton[1] showed that Henry's law holds good when a mixture of gases is absorbed by a liquid. The liquid absorbs each constituent of the mixture, as if that one only were present and exerted a pressure corresponding to its quantity. In dissolving, and also in the solutions produced, mixtures of gases obey the law of addition, which law has been found already to express all their other properties.

3. **Measurement of the quantities absorbed.**—Absorption begins as soon as a gas is brought into contact with a liquid. The surface-layer of the liquid takes up as much of the gas as is possible under the conditions; the gas absorbed then passes to the interior of the liquid by diffusion, and the surface-layer dissolves more. This process is repeated till the liquid is saturated; but as diffusion occurs slowly, a long time elapses before the maximum absorption is attained. By intimately mixing the gas with the liquid, and constantly agitating the liquid, saturation is more quickly reached. When large quantities of a gas are available, saturation may be effected most easily by slowly

[1] *Mem. Manchester Phil. Soc.* 1 [1808].

passing a stream of the gas into the liquid, kept at a constant temperature for some time. In other cases, the apparatus of Bunsen, or some similar apparatus, may be used. Bunsen[1] places the gas in a graduated tube over mercury, adds a measured volume of the liquid, which has been boiled to expel air, fixes the open end of the tube tightly against a caoutchouc-plate, immerses in a cylinder of water (to maintain a constant temperature), and shakes violently for some time. By repeatedly opening the tube under mercury, allowing the mercury to enter, and again shaking, a condition of equilibrium is attained; the volume of gas absorbed by the liquid is determined by measuring the diminution in the volume of the gas, the increase in the volume of the liquid, and the pressure.

Many other pieces of apparatus are in use besides that of Bunsen. One was described by G. Wiedemann,[2] and was improved by Hüfner. The absorption-vessel consists of two chambers, connected by a two-way stopcock, and also connected with a manometer which is quite filled with mercury. One of the chambers is filled with the gas, and the other with the air-free liquid; the manometer is disconnected, the stopcock connecting gas and liquid is opened, the whole is shaken, the manometer is connected, and the mercury corresponding to the diminished pressure is allowed to flow out, and these operations are repeated as often as is necessary. The quantity of gas absorbed is found from the weight of mercury which has flowed from the manometer. Heidenhain and Meyer, and afterwards Setschenoff, connected the absorption-vessel, by means of a flexible capillary tube, with a large manometer filled with the gas, and determined the quantity of gas absorbed by measuring the change of pressure in the manometer. Hüfner[3] pumps the gas out of the liquid in which it has been dissolved, by means of a Sprengel mercury-pump, and determines the

[1] *Annalen*, **93**, p. 10 [1855].
[2] *J. für prakt. Chemie*, **22**, p. 268 [1880].
[3] *Wied. Ann.* **1**, p. 629 [1877].

amount of gas eudiometrically. In many cases the quantity of gas absorbed may be determined by one of the ordinary analytical methods. The gain in weight of the absorption-apparatus gives a direct measurement of the quantity of gas dissolved; this method is frequently applicable.

The following absorptiometer, constructed after that of Heidenhain and Meyer, has been found convenient and accurate in my own laboratory. The tube A is for measuring the gas (fig. 1); this tube is divided into cubic centimetres starting from a point chosen arbitrarily; it is connected, by caoutchouc tubing, with a tube of equal diameter, B; this tube, B, is movable, and by means of it the position can be adjusted of the liquid (mercury or water) which shuts off the gas in the measuring-tube. The gas measuring-tube is connected with the absorption-vessel, C, by a flexible capillary tube of lead (silver or platinum is required in a few cases). The stop-cocks *a* and *b* are three-way cocks; *c* is a simple stopcock. The vessel C is filled with the air-free liquid, and A with the gas (the three-way cock enables this to be done easily); pressure having been equalised, the position of the gas in A is read off; A is brought into connexion with C, and by raising B and opening the stopcock *c* a determinate volume of the liquid is made to flow into a measuring flask; an equal volume of the gas passes into C, and then absorption proceeds, C being shaken constantly. To keep the temperature constant, A and C are surrounded by water, or by vapours of known boiling-points.

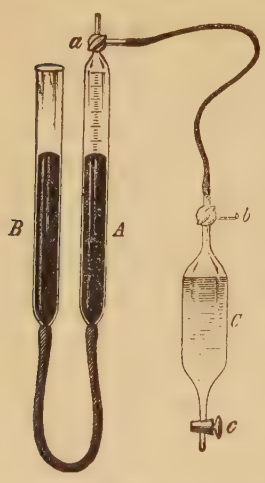


FIG. 1

4. **Absorption-coefficients.**—Bunsen applied the term 'absorption-coefficient' to the volume of gas, reduced to 0° and normal pressure, absorbed by unit-volume of a specified

liquid at normal temperature. Let v = volume of liquid, v = volume of gas absorbed at pressure p and temperature t, then the volume of gas reduced to 0° and 760 mm, v'_0, is $v'_0 = \frac{v\,p}{760\,(1+a\,t)}$, where $a = \cdot00367$ (the coefficient of expansion of the gas). According to Henry's law, $\frac{760}{p}$-fold the quantity of gas would be dissolved at 760 mm. pressure; the reduced volume then becomes $v_0 = \frac{v\,p}{760\,(1+a\,t)} \cdot \frac{760}{p} = \frac{v}{1+a\,t}$. The coefficient of absorption, β, is found by dividing by the volume of liquid, v:

$$\beta = \frac{v}{\mathrm{v}\,(1+a\,t)}.$$

Bunsen's coefficient of absorption expresses the ratio between the volume of gas, reduced to 0°, absorbed at the pressure of the experiment, and the volume of liquid which effects the absorption. It seems advisable to choose a simpler expression than this, and to do away with the reduction to 0°, inasmuch as this is hardly justified by the nature of the process. I use the expression *solubility of a gas*, λ, to signify the ratio of the volume of gas absorbed to the volume of the absorbing liquid, at any specified temperature and pressure:

$$\lambda = \frac{v}{\mathrm{v}}.$$

The relation between the solubility of a gas and Bunsen's absorption-coefficient is $\lambda = \beta\,(1+a\,t)$.

The absorption-coefficient, and also the solubility, of a gas is independent of the pressure, and is dependent on the nature of the gas and the temperature. According to Bunsen and Carius, the absorption-coefficient of hydrogen in water, and of oxygen and carbon monoxide in alcohol, are independent of temperature. But recent measurements in my laboratory have shown that these statements are based

on experimental errors, and that the coefficients in question vary somewhat with temperature.

Dalton supposed that the influence of temperature on the absorption-coefficients of various gases dissolving in the same liquid is proportional to the influence on each gas separately, so that the composition of the gas dissolved by a specified liquid acting on a mixture of gases is independent of the temperature. Dalton's statement is not strictly accurate; nevertheless it is applicable in a general way.[1] The following tables contain absorption-coefficients of several gases, in water, and in alcohol of S.G. ·792 at 20°; the measurements were made by Bunsen and his pupils:—

Temp.	Nitrogen		Hydrogen		Oxygen	
	W.	A.	W.	A.	W.	A.
0°	0·02035	0·1263	0·01930	0·06925	0·04114	0·2840
5	0·01794	0·1244	0·01930	0·06853	0·03628	0·2840
10	0·01607	0·1228	0·01930	0·06786	0·03250	0·2840
15	0·01478	0·1214	0·01930	0·06725	0·02989	0·2840
20	0·01403	0·1204	0·01930	0·06668	0·02838	0·2840

Temp.	Carbon dioxide		Carbon monoxide		Nitrous oxide	
	W.	A.	W.	A.	W.	A.
0°	1·7967	4·3295	0·03287	0·2044	1·3052	4·178
5	1·4497	3·8908	0·02920	0·2044	1·0934	3·844
10	1·1847	3·5140	0·02635	0·2044	0·9196	3·541
15	1·0020	3·1993	0·02432	0·2044	0·7778	3·268
20	0·9014	2·9465	0·02312	0·2044	0·6700	3·025

Temp.	Methane		Ethylene		Sulphuretted hydrogen	
	W.	A.	W.	A.	W.	A.
0°	0·05449	0·5226	0·2563	3·595	4·371	17·89
5	0·04885	0·5086	0·2163	3·323	3·965	14·78
10	0·04372	0·4954	0·1837	3·086	3·586	11·99
15	0·03909	0·4828	0·1615	2·883	3·233	9·54
20	0·03499	0·4710	0·1488	2·713	2·905	7·42

[1] *Vide* E. Wiedemann, *Ladenburg's Handwörterbuch d. Chemie*, 1. p. 4.

Temp.	Nitric oxide	Butane	Ethane
	A.	W.	W.
0°	0·3161	0·03147	0·0871
5	0·2999	0·02689	0·0720
10	0·2861	0·02355	0·0599
15	0·2748	0·02147	0·0508
20	0·2659	0·02065	0·0447

The above numbers comprise almost all the absorption-coefficients of gases in single liquids which have been determined. The numbers cannot be regarded as finally correct. Besides the number given for ethane, C_2H_6, Bunsen's results[1] contain a series of numbers for *äthyl-wasserstoff*, C_2H_6; the numbers differ from eight to ten per cent. from those for ethane (or methyl as it is called in the original memoir); but we know now that there is but one compound having the formula C_2H_6.

Many chemists have thrown doubt on the accuracy of the values given by Bunsen for the absorption-coefficients of oxygen, and have shown that the true values are probably greater than Bunsen's. L. W. Winkler recently gave the following numbers: 0° = ·0489, 5° = ·0429, 10° = ·038, 15° = ·0342, 20° = ·031, 25° = ·0284, 30° = ·0262. These results were obtained by combining the oxygen with MnO and decomposing the MnO_2 formed by KI and hydrochloric acid.[2] Pettersson and Sondén obtained nearly identical results by a volumetric method of analysis.[3]

The remarkable observation that the absorption-coefficients of hydrogen in water and oxygen in alcohol are not affected by changes of temperature has not been confirmed. A very careful series of measurements carried out by W. Timofejeff,[4] with the apparatus described on p. 12, has shown that the coefficients in question decrease with increase of temperature. The numbers are:—

[1] For references *vide Berichte*, **22**, p. 1439 [1889].
[2] *Berichte*, **22**, p. 1439 [1889]. [3] *Ibid.* **22**, p. 1764.
[4] *Zeitschr. f. physikal. Chemie*, **6**, p. 141 [1890].

Temp.	Hydrogen in Water	Oxygen in Alcohol
0°	·0215	·2337
5	·0206	·2300
10	·0198	·2266
15	·0190	·2232
20	·0184	·2201
25	·0178	·2170

The values for oxygen in alcohol differ considerably from those given by Bunsen.

5. **Absorption in other liquids.**—There seems no doubt that Henry's law holds good for all liquids, and is not to be restricted to water and alcohol, the liquids which have been generally used in experiments on absorption-coefficients. Investigations have been made by Woukouloff,[1] with carbon disulphide and chloroform; the results show agreement with Henry's law within the limits of the applicability of the general gaseous laws. No simple relations have been traced, as yet, between the nature of the solvent and the solubility of a gas. The absorption-coefficients of a gas in different solvents are not proportional to one another; this was shown by Bunsen for water and alcohol, and confirmed for petroleum by Gniewosz and Walfisz.[2]

6. **Testing Henry's law.**—Henry himself tested his law, and confirmed its accuracy by examining five different gases at pressures varying from one to three atmospheres. Henry contented himself with a somewhat rough approximation; the experiments could not at that time be very accurate. At a later time, Bunsen and his pupils conducted experiments which confirmed the law. The pressure in Bunsen's absorptiometer could be changed only to a small extent, so that the limits of the experiments were somewhat narrowed; on the other hand the limits of pressure could be extended considerably by using mixtures of gases. In such a case, let there be, in unit-volume of the mixture,

[1] *Compt. rend.* **108**, p. 674; **109**, p. 61 [1889].

[2] *Zeitschr. f. physikal. Chemie*, **1**, p. 70 [1887].

q_1, q_2, q_3 . . . . volumes of the different gases; then the partial pressure of each gas is $q_1 p$, $q_2 p$, $q_3 p$, if p be the total pressure. Then, putting β_1, β_2, β_3 . . . . as the absorption-coefficients of the different gases, the quantities of the gases absorbed g_1, g_2, g_3, ... are, for the unit-volume of the liquid, $g_1 = \beta_1 q_1 \frac{p}{760}$, $g_2 = \beta_2 q_2 \frac{p}{760}$, $g_3 = \beta_3 q_3 \frac{p}{760}$ . . . . It is evident that by decreasing the quantity of a constituent of the mixture, and therefore decreasing the partial pressure, it becomes possible to test the law for pressures between 0 and one atmosphere. As an example, I give experiments made by Bunsen on a mixture containing, by analysis, ·7319 hydrogen and ·2681 carbon dioxide. The composition of the gases absorbed was calculated from the observations by using the absorption-coefficients of pure hydrogen and carbon dioxide.[1]

Three experiments gave:—

	1	2	3	Mean	By Analysis
Hydrogen . . .	·7343	·7372	·7285	·7333	·7319
Carbon dioxide .	·2657	·2628	·2715	·2667	·2681

These numbers indicate the accuracy of the law; but they contain no systematic examination of the sphere within which it is applicable. Bunsen expressed the opinion that there are limits within which the law holds good; but he did not undertake the determination of these limits.

Khanikoff and Luginin[2] carried out measurements to fill up the gap left by Bunsen. These investigators modified Bunsen's absorptiometer, by making it possible to detach the manometer completely when the vessel was being shaken to ensure thorough absorption of the gas; the shaking was done under water by means of a rotating cylinder. The gas used was carbon dioxide; deviations from the gaseous laws were taken into account in reducing to normal temperature and pressure. The results are presented in

[1] *Gasometrische Methoden*, p. 245.
[2] *Ann. Chim. Phys.* (4) 11, p. 412 [1867].

the following table;[1] P = pressure at the end of the experiment, g = volume of gas absorbed, h = volume of water used for absorption, and a = quantity of gas absorbed at pressure P by unit-volume of water:

P	g	h	a	a : P
69·8	3466	3671	0·9441	0·01352
80·9	5268	4534	1·1619	0·01436
128·9	6979	3743	1·8647	0·01447
147·0	10030	4638	2·1623	0·01471
200·2	10854	3733	2·9076	0·01451
218·9	14757	4646	3·1764	0·01452
236·9	13440	3856	3·4857	0·01472
255·4	17490	4708	3·7152	0·01455
273·8	15135	3781	4·0031	0·01463
311·0	20899	4644	4·5006	0·01447

The authors take the first observation as a basis, and then compare the ratios $a_2 : a_1$, $a_3 : a_1$, $a_4 : a_1$ . . . with the ratios $p_2 : p_1$, $p_3 : p_1$, $p_4 : p_1$ . . . . The two series of ratios are not alike; the first series is greater throughout, and shows increasingly greater values than the second; this result is not that required by the law of Henry. The authors conclude that the law is therefore incorrect. But if no special weight is given to one observation more than to another—i.e. if the ratios $a_1 : p_1$, $a_2 : p_2$, $a_3 : p_3$ . . . . . are calculated as is done in the last column of the foregoing table—it is evident that all the experiments, except the first, give accordant results; the deviations are quite irregular, and are evidently due to experimental errors. These experiments, therefore, fully confirm the law of Henry. This result of the experiments has been pointed out by Naccari and Pagliani,[2] and, at an earlier date, also by Setschenoff. The law of Henry has not been tested of late years by experiments covering so wide a ground as those just referred to. Some experiments by Setschenoff will be referred to again. There is also an investigation by Naccari and Pagliani which is not accessible to me; from the abstract,[3]

[1] Without the unwarranted number of decimal places of the original.

[2] *Nuov. Cim.* (3), 7, p. 71 [1880].

[3] *Beiblätter*, 4, p. 510.

I infer that the results confirm the law of Henry, although within narrower limits of pressure than those used by Khanikoff and Luginin. All these measurements were made with carbon dioxide.

7. **Exceptions to Henry's law.**—Very soluble gases show deviations from the law of absorption. Carius[1] felt certain that the law held good for ammonia, from the results of his experiments on mixtures of this gas with hydrogen; but Roscoe and Dittmar[2] showed that the absorption-coefficients determined by Carius were inaccurate, and that the proportions of ammonia absorbed were much more complicated than was supposed by him. The curve in fig. 2 shows the relations between quantity of gas absorbed and pressure; the straight line, required by the law of Henry, is set down for comparison. The operations were made at 0°. Measurements were made by Sims,[3] somewhat later, at different temperatures; the curve becomes simpler at 20°, and the two changes of curvature have disappeared; at 40° the deviations are less marked, and at 100° the absorption of ammonia obeys the law of Henry. Completely similar results were obtained by Watts,[4] by leading mixtures of air and ammonia through a small quantity of water, at a constant temperature, until the water was saturated. The quantity of ammonia absorbed agreed with that calculated from the partial pressure, using the tables of Roscoe and Sims, and showed deviations from Henry's law: the air behaved as if the ammonia were absent.

The results of very accurate measurements with sulphur dioxide agree with those obtained with ammonia. From experiments on the absorption of mixed gases, Schönfeld[5] concluded that sulphur dioxide obeyed the law of Henry; but Sims showed that the law is obeyed only above 40°, and that at temperatures below this the deviations are

[1] *Annalen*, **93**, p. 33 [1855].
[2] *Ibid.* **112**, p. 349 [1859].
[3] *Ibid.* **118**, p. 345 [1861].
[4] *Ibid.* **Supplbd. 3**, p. 227 [1865].
[5] *Annalen*, **95**, p. 1 [1854].

extremely like those shown by ammonia. The observations of Watts show that it does not matter whether the decrease of pressure be accomplished directly, or by admixture of another gas. Even a very absorbable gas, such as carbon dioxide, exerts no specific effect. This is a confirmation, within very wide limits, of Dalton's law of *the superposition of absorptions*; the law was confirmed

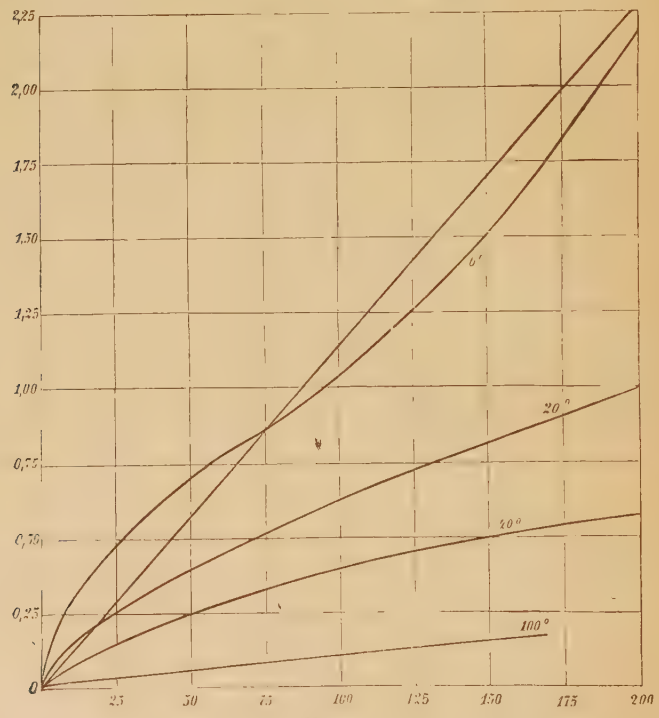


FIG.

by the measurements of Bunsen on mixtures, given above (p. 17), but not in so far-reaching a way as by the present experiments.

Hydrogen chloride shows greater deviations from Henry's law than either ammonia or sulphur dioxide; but this is to be expected, as water and hydrogen chloride react chemically. A marked difference is shown by the fact that

in the curve for hydrogen chloride, when $p=0$, g does not become $=0$, but retains a positive value; i.e. the whole of the gas is not removed from the solution by diminishing the pressure, but some remains, independently of the pressure, and the composition of this residue varies with the temperature. An aqueous solution of hydrogen chloride cannot, therefore, be freed from the gas by boiling, but a liquid distils over of approximately constant composition.

8. **Theory of gas-absorption.**—Dalton regarded the phenomena of absorption as altogether mechanical, inasmuch as they depended on pressure, whereas chemical processes were independent of pressure. He ascribed absorption to the penetration of the particles of gas between the molecules of the liquid; but he could not thus explain why different gases were absorbed in different quantities by the liquid.

Dalton's main argument is not now decisive, as to-day we recognise the influence of pressure on the formation of chemical compounds. The supposition of a simple penetration of the gas-particles between the molecules of the liquid is opposed to the fact—unknown to Dalton—that absorption decreases as temperature increases, although as the total volume of liquid increases the intermolecular spaces must increase also.

Conceptions are arrived at from the molecular theory of liquids[1] which are applicable to the phenomena of gas-absorption. It is certainly to be assumed that attracting forces exist between the molecules of the absorbed gas and those of the liquid; these forces hold fast a definite number of the gas-molecules, which bombard the surface of the liquid, until equilibrium is established between the molecules entering the liquid and those which, by virtue of their energy of motion, again leave the liquid. Under these conditions, the quantity of gas remaining in the

[1] The development of the molecular theory to liquids is discussed by the author in an earlier part of his book.—*Translator.*

liquid must be proportional to the number of molecules passing out of the liquid—that is, proportional to the density, as is required by the law of Henry. If temperature is increased, the gas being maintained under the same pressure, so that the total energy of the molecular impacts on the surface of the liquid remains unchanged, the number of molecules leaving the liquid is reduced in proportion as the energy is increased, i.e. the number of molecules leaving the liquid decreases inversely to the absolute temperature. This explains the decrease in the absorption-coefficients with rise of temperature to some extent, but not fully, as the decrease is found to be much larger than this explanation predicts.

There is undoubtedly a decrease of the attraction of the liquid, and this soon shows itself in the vapour of the liquid, inasmuch as the pressure of the vapour increases much more rapidly than in proportion to the absolute temperature. At all events, it is evident that the influence of the liquid is much greater than that of the gas on the change in the absorption-coefficient, which is connected with change of temperature, and that, thus, there is an approximate proportionality between the quantity of gas absorbed and the temperature-coefficient.

The question as to the state of aggregation of the absorbed gas belongs to those questions which are made more difficult to answer by reason of the vagueness of their meaning. Inasmuch as a gas-solution is a physically homogeneous liquid, the gas contained therein must be said to be in the liquid state; but, inasmuch as the critical temperatures of many gases lie more or less below the temperature at which absorption is carried out, it cannot be supposed that such gases are so attracted by the liquid that they are first liquefied and then dissolved, as Graham supposed. The absorbed gaseous particles form a part of the liquid just as truly as the molecules of the liquid itself; but the absorbed gas is not a liquid within the solvent. In the cases of gases whose critical temperatures are above that of

the experiment, mutual reactions between the absorbed molecules come into play, especially when much gas is dissolved. This is the case, e.g., with ammonia; one must suppose that the molecules of ammonia are in a condition similar to that which occurs when ammonia is liquefied by pressure. The deviations of such gas-solutions from Henry's law are explained by this assumption; and the assumption also indicates that increase of temperature ought to decrease the deviations, both by decreasing the quantity of gas absorbed and also by bringing the gas nearer its critical point. Unfortunately, there are not sufficient data concerning the effect of temperature on the absorption of gases to verify this hypothesis numerically.

Wroblewski's experiments on the process of gas-absorption must be mentioned here. Wroblewski was concerned for the most part with the diffusion of dissolved gases through the solvent, but he also made use of his experiments to gain an insight into the nature of the process of solution.[1] He found that the diffusion of the absorbed gas through the solvent follows the same law as the diffusion of other dissolved bodies; the quantity diffused through a specified cross-section is proportional to the difference of concentration of the adjacent layers, and is dependent on the nature both of the gas and of the solvent. The character of the law was found to be the same whether water, a saline solution, viscid jelly, or caoutchouc, was used. The rate of progression of the dissolved gas in the medium was found by Wroblewski to be nearly inversely proportional to the square root of the specific gravity of the gas; in other words the rate of progression was nearly proportional to the rate of movement of the molecules. From these results Wroblewski concludes that gases retain their state of aggregation when they are absorbed by liquids. This conclusion appears to me to be erroneous. To conclude, from the experiments in question, that a dissolved gas is not liquefied, it is necessary to assume that the rate of movement of the

[1] *Wied. Ann.* **8**, p. 29 [1880].

molecules of the liquid is *not* inversely proportional to the square root of the molecular weight; but the opposite of this is probably true, i.e. it is probable that the proportionality in question holds good for liquids.

9. **Absorption of gases by saline solutions.**— The investigation of the behaviour of gases towards solutions of salts was begun in order to answer certain physiological questions, especially those concerning the absorption of carbon dioxide by blood-serum.

Overlooking an observation made by Pagenstecher,[1] to the effect that a solution of sodium phosphate absorbs more carbon dioxide than water, and holds the absorbed gas more firmly, Marchand[2] and Liebig[3] took up the inquiry, but they failed to gain a basis of experimental facts sufficiently wide to solve the physiological questions at issue. Liebig found that, especially in the case of ordinary sodium phosphate solution, a part of the carbon dioxide reacts chemically with the dissolved salt, while another part is dissolved as in water; the latter portion follows the law of Dalton, the first portion does not obey this law.

The subject was taken up by Fernet,[4] in the year 1858, in an extended series of experiments having primary reference to physiological inquiries; a year earlier L. Meyer[5] had investigated the absorbent action of the liquids of the blood. From his measurements, Fernet concluded that the absorption is conditioned by the nature both of the gas and the dissolved salt; and that this conditioning influence is exerted in two directions. Henry's law holds good in the cases of gases which exert no chemical action on the dissolved salt: for instance, in the absorption of carbon dioxide, oxygen, or nitrogen, by a solution of common salt, the absorption-coefficients are only somewhat smaller than if pure water is used. On the other hand, if the gas exerts a chemical action on the dissolved salt, as carbon dioxide does

[1] *Buchner's Repert.* **22**, p. 318 [1840].
[2] *J. für prakt. Chemie*, **37**, p. 321 [1846].
[3] *Annalen*, **79**, p. 112 [1851].
[4] *Compt. rend.* **46**, p. 620.
[5] *Pogg.* **102**, p. 299 [1857].

on disodium phosphate or on normal sodium carbonate, then, besides the quantity of gas dissolved in accordance with the usual law of absorption, another quantity of gas is taken up by the solution; this second quantity is independent of the pressure, and is proportional to the quantity of salt in solution; according to Fernet, it bears a simple molecular proportion to the salt present in solution.

Some of Fernet's results were called in question by Heidenhain and L. Meyer.[1] These experimenters asserted that the behaviour of ordinary sodium phosphate is much more complex than Fernet's results indicated. It is true, said Heidenhain and Meyer, that the total quantity of carbon dioxide, A, absorbed by volume h of the solution can be expressed by the equation $A = h\,(k + a\,p)$, where k = the portion that reacts chemically and a = the portion which follows Dalton's law; but the values of k and a vary considerably both with concentration and temperature, in the direction that both decrease as temperature increases, and both increase as concentration increases. The results are rightly attributed by Heidenhain and Meyer to the chemical action between carbon dioxide and disodium phosphate.[2] The sharp criticism to which Fernet's work is subjected is noticeable. Fernet's results differed considerably from those of Heidenhain and Meyer, and also from the older measurements; 'this,' say the authors in question, 'is the more remarkable, as Fernet's numbers show an agreement between calculation and observation to less than $\frac{1}{10}$ mm. in pressure and $\frac{1}{100}$ cc. in volume. This agreement extends even to cases where, from an oversight, an entirely erroneous value has been taken as the basis of the calculation. Considering all things, we cannot accept Fernet's work as an unvarnished record of results obtained by actual experiments.'

The problems remained untouched for ten years, and

[1] *Annalen*, **Supplbd. 2**, p. 157 [1863].

[2] This action is discussed by the author in that part of his book which deals with chemical affinity.—*Translator.*

were then taken up by isolated experimenters, whose researches are noticed in chronological order in the following paragraph.

10. **More recent work.**—The absorption of ammonia by salt solution was examined by Raoult[1] in 1873. The following results are selected from his memoir. Raoult began with experiments on the absorption of ammonia by pure water; the conclusions confirmed those of Roscoe and Dittmar, which differed from the results obtained by Carius. Experiments were then made with potash solution; several flasks with different solutions were placed in the same water-bath, and a stream of ammonia was passed into them for two hours. The results showed that solubility decreased as the potash increased, and decreased in proportion to the quantity of potash present. The table shows some of the results; the numbers in the last column are calculated from those in the second and third columns, assuming the proportionality between quantity of potash and quantity of gas absorbed :—

Temp.	Water	Solution with 11·25 per cent. K_2O	Solution with 25·25 per cent. K_2O	
0°	90·0	72·0	49·5	49·68
8	72·75	57·0	37·5	37·47
16	59·75	46·0	28·5	28·95
24	49·5	37·25	21·75	22·06

Further experiments gave similar results; the agreement between the quantities of gas absorbed and potash present was maintained up to 30 per cent. potash ($KOH + 7H_2O$); after that point more gas was absorbed than the proportionality demanded. Experiments with soda gave quite similar results: potash and soda solutions of equal concentrations absorbed equal quantities of ammonia. Solutions of ammonium chloride absorbed slightly less ammonia than equal volumes of water; these solutions followed the law of proportionality until they were saturated.

[1] *Ann. Chim. Phys.* (5), 1, p. 262.

Solutions of sodium nitrate and ammonium nitrate absorbed exactly the same quantities of ammonia as equal volumes of water. At 13° and 760 mm. the following results were obtained :—

100 cc. water absorbed	64·5	grams ammonia
100 cc. 74·1 p. ct. ammonium nitrate solution absorbed	63·75	„ „
100 cc. 52·4 p. ct. sodium nitrate solution absorbed .	64·25	„ „

On the other hand, solutions of calcium nitrate absorbed more ammonia than water ; in this case the law of proportionality was followed :—

Temp.	Water	Solution of 28·38 p. ct.	Solution of 59·03 p. ct.	
			Observed	Calculated
0°	90·0	96·25	104·5	103·0
8	72·75	78·5	84·75	84·65
16	59·5	65·0	70·5	70·88

Raoult mentions that these noticeable results may be explained by supposing that the ammonia seizes on a portion of the acid, but he thinks this supposition is refuted by the fact that the residue obtained by evaporation was free from ammonia. But this is really no evidence against the existence of ammonium nitrate, along with lime, in the solution ; inasmuch as ammonia and calcium nitrate would be formed again on evaporation.

Using an improvised mercury-calorimeter, Raoult found that the quantities of heat produced during absorption were nearly independent of the nature of the absorbing liquid. Thus 1 gram ammonia dissolving in the following liquids produced the quantities of heat [1] noted :—

	Units of heat
Water	492
Calcium nitrate solution (S. G. 1·208)	487
Ammonium nitrate solution (S. G. 1·275) . . .	483
Potash solution (S. G. 1·261)	479

[1] The unit of heat adopted by Ostwald is the quantity of heat given out when 1 gram of water cools from 100° to 0°.—*Translator.*

These results are of great interest; further measurements were promised by Raoult, but none have yet been published.

11. **Salt-solutions.**—Investigations similar to those made by Raoult were published, a few years later, by Setschenoff,[1] and also by Mackenzie.[2] Mackenzie confined himself to establishing certain empirical relations. Setschenoff went much more deeply into the nature of the phenomena. He recognised the existence of two classes of salts: those which absorb a part of the carbon dioxide independently of Henry's law, e.g. sodium carbonate, disodium phosphate, borax, &c.; and those which exert no definite chemical action on the carbon dioxide, e.g. nitrates, chlorides, and sulphates. If the absorption-coefficients are regarded as functions of the concentration, and these coefficients are represented as the ordinates of a curve, the abscissæ of which are formed by the concentrations, then salts of the first kind show a rise of absorption-coefficient with rise of quantity of salt, following on the combination of carbon dioxide in proportion to the quantity of salt, whereas salts of the second kind show a fall in the curve, inasmuch as more concentrated salt solutions absorb less carbon dioxide than those of less concentration. The two classes of salts cannot be very decidedly marked off from one another. The order for salts of sodium is given by Setschenoff thus:—

Sodium carbonate . . Na_2CO_3	Sodium oxalate . . . $Na_2C_2O_4$
Borax . . . . . $Na_2B_4O_7$	Sodium lactate . . . $NaC_3H_5O_3$
Disodium phosphate . Na_2HPO_4	Sodium nitrate . . . $NaNO_3$
Sodium acetate . . . $NaC_2H_3O_2$	Sodium chloride . . . $NaCl$
Sodium citrate . . . $Na_3C_6H_5O_7$	Sodium sulphate . . . Na_2SO_4

The division of the classes occurs at sodium oxalate. There is another difference to be noted: in the first group the quantity of carbon dioxide chemically held, not in obedience to the law of Henry, is equivalent to the quantity of salt (this was noticed by Fernet); in the other salts there

[1] *Mem. Akad. Petersb.* **22**, No. 6 [1875]. [2] *Wied. Ann.* **1**, p. 438 [1876].

is no proportionality of this kind, the amount of carbon dioxide held chemically is smaller, and increases in proportion to the quantity of salt, if the solution is dilute. The phenomenon is certainly conditioned by the chemical affinity between carbonic acid and sodium, and is modified by the greater or less stability of the salts. The further discussion of the matter does not belong to the present subject; it is only necessary to remark here that the magnitudes of the absorptions by salts of the first kind appear as the sums of two actions, one of which is chemical and one is simple absorption. In the second class of salts, chemical absorption disappears, and the dissolved carbon dioxide follows the law of Henry. Traces of chemical absorption occur in the salts placed at the top of the list of this class. The absorption-coefficients decrease with increasing concentration. Setschenoff found that solutions of equivalent quantities of similar salts of the same acid absorbed equal quantities of carbon dioxide, and were therefore 'absorptiometrically equivalent.' For instance, different solutions of magnesium sulphate and zinc sulphate showed the following absorption-coefficients:—

Magnesium sulphate . . .	·713	·587	·523
Zinc sulphate	·715	·593	·522

The following values were also obtained:—

Barium nitrate . . .	·922	Strontium chloride . .	·892
Calcium nitrate . . .	·923	Sodium sulphate . . .	·670
Strontium nitrate . . .	·916	Copper sulphate . . .	·672
Barium chloride . . .	·894		

Setschenoff thinks that the effect exerted by these salts, and salts like these, on the absorption of carbon dioxide, is to be traced to the decomposition of the salts by the water; but if this is so, no answer is found to the question why the amount of absorption is *smaller* than corresponds with the water present in the absorbing volume of the solution. It is to be wished that experiments were made with a gas which would exert no chemical action on the salt in

solution; nitric oxide might be used, as the quantities of the gas absorbed are nearly the same as those of carbon dioxide. More recently, Setschenoff[1] has considerably widened his investigations, and has brought them to a conclusion for the time. It is shown that the absorption-coefficients of salt-solutions are smaller than those of water, and that the absorption follows Dalton's law. The connexion between the quantity of salt, x, and the absorption-coefficient, y, is thus expressed by Setschenoff—

$$y = a\, e - \frac{k}{x}$$

where a = absorption-coefficient for water, e = basis of the natural logarithms, k = a constant dependent on the nature of the dissolved salt.

This formula does not represent the absorption-coefficients quite accurately: there are small deviations, which Setschenoff refers to secondary influences. Conclusions may be drawn from these phenomena regarding the nature of salt-solutions; but this is not the place to discuss these conclusions. One empirical result is noteworthy, viz. that solutions containing equivalent quantities of similar salts have nearly equal absorption-coefficients. This statement cannot be applied at present to all salts. The statement that if salts of the same metal with different acids are arranged in order of the absorption-coefficients of their equivalent solutions, this order is the same whatever be the metal, holds good in all cases; so also, all salts of the same acid, with different metals, follow the same order, whatever be the acid. The influence of the salt on the absorption is, thus, truly an *additive property*.[2] Some other

[1] *Nouv. Mém. de la Soc. des Natural. Moscou*, **15**, Livr. 6 [1889]; abstract in *Zeitschr. f. physikal. Chemie*, **4**, p. 117 [1889].

[2] The author distinguishes *additive*, *constitutive*, and *colligative*, properties. *Additive* properties are those which are the sums of the properties of the constituents; these properties are not affected by the chemical combination of the constituents of a substance. The mass of a compound, for instance, is a purely additive property. Few properties are entirely additive.

investigations have been made into the absorption of gases by salt-solutions, but no results of general applicability have been obtained. Buchanan [1] measured the solubility of carbon dioxide in solutions of calcium and magnesium sulphates; varying results were found according as the solutions were freshly prepared or were allowed to remain saturated with the gas for some days. The investigations of Kumpf [2] and of Goodwin [3] have not led to any far-reaching conclusions. The whole problem will approach solution when the behaviour towards salt-solutions of gases which exert no chemical action on the solutions is studied carefully and exhaustively.

12. **Solutions in mixed liquids.**—From a series of experiments on the absorption of carbon dioxide in sulphuric acid, Setschenoff [4] drew the noteworthy conclusion that the absorption-coefficient of pure sulphuric acid is the same as that of water, and that the coefficient of the acid rapidly decreases on adding water. A minimum value is found for the acid approximately of the composition H_2SO_4, H_2O; the absorption then increases on addition of water. The values were as follow:—

H_2SO_4	$+\frac{3}{10}H_2O$	$+\frac{1}{2}H_2O$	$+H_2O$	$+2H_2O$	$+58H_2O$
·923	·852	·719	·666	·705	·857

Setschenoff seeks for an explanation in the fact that the absorption of the carbon dioxide and the hydration of the

Properties which are dependent on the arrangement of the constituents of a substance, or on its constitution, are called *constitutive*; the boiling-point of a chemical compound is partly an additive, partly a constitutive, property; the optical activity of a compound is a constitutive property. A third group of properties, the connexion of which with the nature of this or that substance is neither of an additive nor a constitutive character, are called *colligative*: these properties have equal values for chemically comparable quantities of the most different substances. The volume occupied by a homogeneous substance in the gaseous state is a colligative property; chemically comparable quantities of the most different gaseous substances have equal volumes.—*Translator.*

[1] *Proc. R. S.* **22**, pp. 192, 483 [1874].

[2] *Dissertation*, Graz, 1881; abstract in *Beiblätter* for 1882, p. 276.

[3] *Berichte*, **15**, p. 3039 [1882].

[4] *Mém. Akad. Pétersb.* **22**, p. 102 [1876].

sulphuric acid proceed equally. O. Müller[1] made very similar observations with mixtures of water and alcohol. The addition of alcohol to water causes a decrease in the absorptive power of the liquid, although alcohol has a much larger absorption-coefficient than water; a minimum is reached on adding more alcohol, and the absorption then increases until it reaches the value for pure alcohol. The minimum is situated at about 30 per cent. alcohol by weight; the experiments were not accurate enough to fix the minimum with certainty. O. Lubarsch[2] found very similar results in studying the absorption of oxygen, hydrogen, and carbon monoxide, by aqueous alcohol; at about 30 per cent. each absorption-coefficient reached a minimum. These facts show in a marked way the great influence which is exerted on the value of an absorption-coefficient by the nature of the liquid.

13. **Volume-changes of the liquid during the absorption of gases.**—The earliest accurate measurements of the changes of volume and specific gravity which liquids undergo, when they absorb gases, were made in the last quarter of the eighteenth century by Bergmann.[3] In the early years of the present century, Thomson found that 1 volume water, on saturation with ammonia, becomes 1·666 vols., and becomes 1·5 vols. on saturation with hydrochloric acid, 1·04 vols. with sulphur dioxide, and 1·002 vols. with chlorine. Nothing more was done until 1863, when Deicke[4] examined the change of volume which accompanies the absorption of hydrochloric acid by water. Deicke's memoir has no general interest; the numbers he found were smaller than those of Thomson; the volume-change accompanying saturation was 48·7 per cent. of the water employed at 0°, and 42·3 per cent. at 23°. Mackenzie and Nichols[5] conducted experiments on the changes of volume which water undergoes when it absorbs a gas, such as carbon dioxide, which

[1] *Wied. Ann.* **37**, p. 24 [1889].
[2] *Ibid.* **37**, p. 524 [1889].
[3] *Opusc.* **1**, p. 9.
[4] *Pogg.* **119**, p. 156 [1863].
[5] *Wied. Ann.* **3**, p. 134 [1878].

is only slightly soluble. The apparatus consisted of a flask completely filled with water, and having a smaller flask attached by a tube fitted with a stopcock. The smaller flask was weighed before the absorption began, and again at the close of the experiment; the increase in weight gave the increase in volume of the water (the smaller flask was furnished with a calcium chloride tube, to prevent loss of water-vapour). It appeared that the expansion of the water, consequent on saturation with carbon dioxide, was proportional to the absorption-coefficient—in other words, was proportional to the quantity of gas; the expansion amounted to ·002144 of the total volume at 2°, and to ·00101 at 32°; the expansion diminished (like the absorption-coefficient) as temperature increased. The absorption-coefficient was 1·002 at 15°, the expansion was ·001378. If this is calculated as entirely due to the carbon dioxide, the specific gravity of this compound becomes about 1·437 (as 1·002 litres $C O_2$ = 1·987 millgm.); this number is more probably too large than too small.

K. Ångström extended the measurements to a greater number of gases.[1] He used a large dilatometer connected with the lower part of the vessel in which the absorption proceeded, and bent so as to be parallel with this vessel. The dilatometer was filled with water and mercury; by warming and cooling, a measured quantity of gas was brought into the vessel; after absorption and establishment of the original temperature (0°), the increase in volume was read off directly on the dilatometer-tube. The results obtained showed that the increase in volume attending successive additions of gas was proportional to the quantity of the gas; the same result had been arrived at previously by Nichols and Mackenzie for carbon dioxide, and by Nichols and Wheeler[2] for ammonia. The gases examined by Ångström were air, oxygen, hydrogen, carbon monoxide and dioxide. The smallness of the differences between the increases in a specified volume of water, when it absorbs

[1] *Wied. Ann.* 15, p. 297 [1882]. [2] *Phil. Mag.* (5), 11, p. 113 [1881].

different gases, is noteworthy. The following numbers are given by Ångström; they represent the relative increments of volume following the absorption by the liquid of a volume of gas equal to its own volume :—

Nitrogen	·00145	Oxygen	·00115
Air	·00140	Hydrogen	·00106
Carbon monoxide . .	·00127	Carbon dioxide . . .	·00125

The corresponding values for a very soluble gas approach these numbers, but all of them are somewhat smaller. From these results it would follow that the specific gravity of the absorbed gas is nearly proportional to its specific gravity in the free state.

Ångström traces a connexion between the compressibility of the gas and the increase in volume of the solvent; the less compressible gases produce greater volume-increments. As the pressures which correspond with the decrease in volume of the gases consequent on absorption amount to from 2,000 to 3,000 atmospheres, only a portion of Natterer's measurements are available in these cases. The relation in question can be shown at present only approximately. The examination of the relation of these results to the molecular volume of the gas (b in the equation of van der Waals, see p. 7) is of great interest. A comparison with the value calculated by the formula of van der Waals (p. 7), or a corresponding formula given by Clausius, shows certain analogies and also differences. I give the values: δ = expansion on absorption :—

	δ	b
Oxygen	·00115	·00089
Nitrogen . . .	·00145	·001359
Hydrogen . . .	·00106	·000887
Carbon dioxide . .	·00125	·000866

At a later time Ångström examined the absorption by liquids other than water.[1] The following table gives the results in the same form as was used in stating the results for water (*see above*) :—

[1] *Wied. Ann.* **33**, p. 223 [1888].

	Carbon dioxide	Air	Hydrogen
Chloroform . . .	·00188	·00205	·00160
Nitrobenzene . .	·00168	—	—
Water	·00130	·00143	·00106
Benzene . . .	·00200	·00216	·00170
Methyl alcohol . .	·00184	·00201	·00157
Ethyl alcohol . .	·00185	·00203	·00152
Ether	·00200	·00240	·00182

The numbers in the three columns are nearly proportional, so that the volume-increments caused by the three gases in the different liquids are in the same ratio, and this is independent of the nature of the liquids. In these cases also, as in that of water, the smallness of the differences for the same liquid are noteworthy.

It is well known that aqueous solutions of the easily absorbed gas, hydrogen chloride, bromide, iodide, &c., show contraction of volume on dilution with water; in these cases the expansion attendant on absorption cannot be proportional to the quantity of gas absorbed, but must increase more slowly than the latter.

CHAPTER III

SOLUTIONS OF LIQUIDS IN LIQUIDS

1. **Generalities.**—In contradistinction to gases, each of which can mix with every other to form an externally homogeneous whole, liquids show remarkable differences in their behaviour to one another, and these differences are dependent upon the nature of the liquids. Pairs of liquids may be divided into three classes. Those in the first class behave in the same way as gases; the solubility of one in the other is unlimited, and the liquids form homogeneous mixtures in all proportions: water and alcohol, chloroform and carbon disulphide, are examples of such liquids. Those in the second class dissolve one another, but not in all proportions. For instance, ether dissolves in water; but when more than one part ether is added to ten parts water, the excess of ether remains separate from, and insoluble in, the aqueous liquid. Similarly, ether dissolves about 3 per cent. of water; there is a limit which cannot be passed by adding larger quantities of water. A solution of a little ether in water behaves towards other liquids like water; a solution of water in ether shows the general properties of ether. Those pairs of liquids which are placed in the third class exert no mutual solvent action. There are very few combinations of liquids which belong strictly to this category. All those liquids must be excepted which show an appreciable vapour-pressure at the temperature of experiment. For, inasmuch as, speaking generally, all gases are soluble in liquids, a similar behaviour must be predicated of all vapours, from which follows the power

of one liquid to dissolve the vapour of another liquid. But a solution of the vapour is not to be distinguished from a solution of the liquid itself. The fact that water, which does not mix with volatile oils, acquires the smell of these oils when shaken with them, shows that the water dissolves some part, although it may be a very small part, of the oil. The division between the second and third classes varies, and is dependent to some extent on the fineness of the methods of analysis. In the same way, the division between the first and second classes is not fixed, but is dependent on the temperature. Liquids which are partially soluble at a specified temperature are sometimes wholly miscible at other temperatures.

2. **Solutions of the first kind.**—The properties of a mixture of liquids, speaking generally, are not those which the mixture would possess, did each constituent exert an influence proportional to its quantity. For instance, the volume of a mixture of liquids is not the sum of the volumes of the constituents, but is generally smaller than the sum; similarly with the optical, thermal, and other properties. To illustrate these points, I append a series of numbers, determined by Dupré, for a mixture of methyl alcohol and water[1]:—

Percentage of Alcohol	Spec. heat. Diff.	Capillarity. Diff.	Sp. gravity at 10°. Diff.	Compressibility. Diff.
10	+·0275	−·254	+·0087	−·0000113
20	·0425	·294	·0186	194
30	·0516	·296	·0265	276
40	·0589	·271	·0312	298
50	·0548	·235	·0326	350
60	·0518	·178	·0313	349
70	·0467	·133	·0275	342
80	·0334	·087	·0208	267
90	·0129	·043	·0114	141

The numbers under *Diff.* represent the differences between the observed values and those calculated on the assumption that each constituent influences the properties

[1] *Proc. R. S.* 20, p. 336 [1872].

in proportion to its quantity. The values for pure water are taken as unity, except in the last column, where the ordinary compression-coefficients are used. No regularity has yet been discovered in the deviations. Certain combinations of liquids, especially those of alcohol and water, have been examined very carefully without the discovery of any law expressing the influence of the quantity of either constituent on the properties of the mixture. The phenomena are extremely complicated; in some cases the direction of the deviations from the calculated mean is dependent in a marked way on the temperature.

Instructive examples of the behaviour of these mutual solutions of liquids are to be found in the researches of Bussy and Buignet.[1] Water, alcohol, ether, acetic acid, carbon disulphide, chloroform, and turpentine were examined; no pair of these liquids mixed without change of temperature. The temperature-changes were sometimes positive, sometimes negative; even with the same pair of liquids the change of temperature in some cases changed its sign. The numbers given in the memoir represent differences of temperature only, hence comparisons cannot be made between the quantities of heat produced; but it may be noted that the greatest lowering of temperature (5·6°) occurred on mixing equal volumes of alcohol and carbon disulphide, and the greatest rise (14·4°) occurred with ether and chloroform, while ether and turpentine mixed with scarcely appreciable change of temperature. Six equivalents of chloroform mixed with one equivalent of alcohol with a fall of temperature = 2·5°; when the proportions were $1\frac{1}{3}$: 1 equiv. no change of temperature occurred; and the mixture of 1 equiv. chloroform with 4 equivs. alcohol was attended with a rise of temperature = 4·65°.

Changes of volume occur along with changes of temperature; these are sometimes positive and sometimes negative, i.e. the substances sometimes expand and sometimes contract. The volume of the mixture is generally

[1] *Ann. Chim. Phys.* (4), **4**, p. 5 [1865].

smaller than the sum of the volumes of the constituents; in a few cases there is an increase of volume, e.g. in mixing alcohol with carbon disulphide, or chloroform with carbon disulphide. It cannot be affirmed that there is an ascertainable connexion between the thermal change and the change of volume, inasmuch as there are mixtures which contract and produce heat, and there are also mixtures which contract and at the same time become colder. F. Guthrie [1] examined many cases; no generalisation could be deduced.

One can only guess as to the causes of these phenomena, and as to the ways in which the molecules of liquids act on one another when solution occurs. It is evidently a condition of miscibility that the work required to break through the common separating surface should be less than the mean kinetic energy of the molecules of the liquids; when this is so, the separating surface must disappear. There appear to be forces of attraction between the heterogeneous molecules; but of the nature and magnitude of these forces nothing is known.

3. **Solutions of the second kind.**—The number of those liquids which are miscible only within definite limits is much greater than that of those which mix in all proportions. The process is always reciprocal: a liquid which can dissolve another partially, is also always taken up, more or less, by this other liquid. For instance, a mixture, in arbitrary proportions, of water and ether is separated, by shaking, into two layers, the lower of which (the aqueous solution) contains 10 per cent. ether, while the upper (the ethereal solution) contains 3 per cent. water; it is only when one of the constituents falls below these limits that a single layer is formed. The number of memoirs concerning such liquids is not great. Abascheff [2] seems to have been the first to carry out researches of a general kind in this direction.

[1] *Phil. Mag.* (5), **18**, p. 495 [1884].

[2] *Recherch. sur. la Dissol. mut. des Liquides*: Moscow, 1857.

As this memoir is inaccessible to me, I can state only what is to be found in the abstract.[1] According to this author, liquids which are only partially miscible at low temperatures are sometimes completely miscible at higher temperatures. The numerical data do not seem to be very accurate (e.g. ether is said not to dissolve any water); I append a few, which are given for the ordinary temperature :—

100 vols. water dissolve 9·5 vols. ether
„ water dissolve 9·0 vols. ethyl acetate
„ alcohol (·829) dissolve 40 vols. turpentine
„ alcohol (·829) dissolve 40 vols. carbon disulphide
„ ether dissolve 0 vols. water
„ ethyl acetate dissolve 5 vols. water
„ turpentine dissolve 8 vols. alcohol
„ carbon disulphide dissolve 7 vols. alcohol.

Abascheff found that solution was attended now with rise, and now with fall, of temperature.

Another Russian investigator, W. Alexejeff,[2] has published further experiments. He finds very complicated relations: for instance, the solubility of amyl alcohol in water decreases as temperature rises, but the solubility of water in this alcohol increases with increase of temperature: the solubility of butyl alcohol in ethyl acetate decreases as temperature increases; but there is a minimum, after which the mutual solubility increases. Phenol becomes more soluble in water as temperature is increased; at 80° the liquids mix in all proportions. Complete miscibility is reached in many cases at high temperatures;[3] water and isobutyl alcohol mix in all proportions at 116°–123°, water and cresol at 118–119°, water and aniline at 114°. This last result is to be found in a more recent contribution,[4] where it is said that the statement holds good for all liquids which dissolve one another; bromine and ether in

[1] *Jahresber.* 1858, p. 52.

[2] *Berichte*, **8**, p. 265; **9**, pp. 1442, 1810; **12**, p. 2172: collected together in *Wied. Ann.* **28**, p. 305 [1886].

[3] *Chem. Centralblatt*, 1882, p. 763.

[4] *Ibid.* 1882, p. 328.

water are exceptions, because these liquids vaporise before complete miscibility is reached.

It is to be noted here that van der Waals deduced the complete miscibility of all liquids, under certain conditions, one of which was a sufficiently great pressure: according to Alexejeff, however, pressure exerts no special effect. The whole phenomena remain, as yet, in the first stage of their elucidation.

It may be urged on behalf of the conclusion arrived at by Alexejeff that the miscibility of gases is independent of the nature of the gases; and that this property seems to be retained at the critical points. Hence it may be supposed that when liquids approach the gaseous state by being heated they will also approach the condition of complete miscibility. The views of van der Waals are not really in opposition to those of Alexejeff.

The observations which Alexejeff made with salicylic acid are especially interesting.[1] This acid melts at 151°; when placed under boiling water it becomes liquid and combines with the water; and when this liquid is heated with water in a sealed tube a few degrees above 106°, it becomes miscible with the water in all proportions; on cooling, liquid hydrated acid separates from the water, and on standing, this acid crystallises. From all the solutions formed by heating above 100°, when sufficiently saturated, the liquid acid separates; but the crystalline acid separates from solutions made at the ordinary temperature; the solubility of the liquid acid is therefore much greater than that of the crystalline acid.

The curves of fig. 3 give a picture of the behaviour of partially miscible liquids. The abscissæ represent temperature; the ordinates, percentages of the dissolved substances in 100 parts of the solution. Solution of water and phenol = a; water and salicylic acid = b; water and benzoic acid = c; water and aniline phenolate = d; water and aniline = e. It is seen that there are always two

[1] *Chem. Centralblatt*, 1882, pp. 677, 763.

definite proportions of the substances corresponding with a state of equilibrium at low temperatures; the solution with smaller ordinates is the solution of the substance in water, that with larger ordinates is the solution of water in the molten substance.

The two solutions become more alike as temperature increases, until they are identical; from that point the liquids are completely miscible. The two branches of the curves may have different positions; it is especially noticeable that, in some instances, the lower branch at first falls till it reaches a minimum, after which it rises.

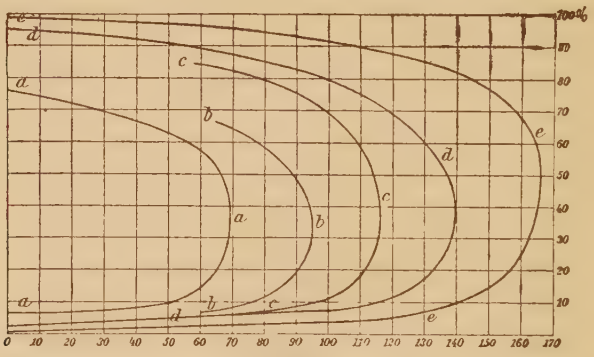


FIG. 3

The method by which Alexejeff determined the mutual solubilities of liquids is very convenient. In place of preparing a saturated solution at a specified temperature, and analysing this, he placed weighed quantities of the liquids in a sealed tube, and, by repeatedly heating and cooling, he determined the temperature at which the contents of the tube became homogeneous. The general form of the curve of solubility can be ascertained by the performance of a few rough experiments, and then it is easy to choose proportions such that accurate estimations can be obtained.

4. **Evaporation of mixtures of liquids.**—The three kinds of pairs of liquids which have been considered in reference to their mutual solubilities, differ also in reference to their

vaporisation. Liquids which do not mix do not influence one another in their evaporation. As shown by Magnus and Regnault, the vapour-pressure in these cases is equal to the sum of the vapour-pressures of the individual liquids at the temperature of experiment. The saturated vapours of such liquids follow Dalton's law of partial pressures: neither liquid exerts any effect on the vapour of the other.

The following table, from Regnault's measurements,[1] shows the limits within which the law is applicable:—

MIXTURES OF CARBON DISULPHIDE AND WATER

Vapour Pressures

Temp.	Water	Carbon disulphide	Sum	Mixture	Diff.
8°85	8·48 mm.	189·2 mm.	197·7 mm.	196·8 mm.	0·9 mm.
12°07	10·51	216·7	227·2	225·9	1·3
18°85	16·20	285·2	301·4	299·5	1·9
26°87	26·32	388·7	415·0	412·3	2·7

WATER AND BENZENE

Temp.	Water	Benzene	Sum	Mixture	Diff.
10°10	9·23	47·0	56·2	54·9	1·3 mm.
15°26	12·91	60·5	73·4	72·3	1·1
19°88	17·26	75·7	93·0	91·5	1·6
22°53	20·30	86·0	106·3	104·3	1·5

The sums of the separate vapour-pressures agree to about 1 mm. with the vapour-pressures of the mixtures; the latter are always a little smaller; this agrees with the fact, noticed by Regnault, that deviations of the same order of magnitude as these occur in the vapour-pressures of single liquids when vaporised in gases.

By reason of the applicability of Dalton's law of partial pressures, the behaviour of non-miscible liquids on boiling and distilling is perfectly definite. The temperature of the boiling mixture is that at which the sum of the vapour-

[1] *Pogg.* **93**, p. 570 [1854].

pressures of both parts is equal to the outside pressure; this temperature is therefore necessarily lower than that at which the more volatile liquid boils. The last-mentioned fact does not generally become apparent by simply heating the mixture, because it is readily prevented from boiling, and it bumps vigorously; also, should the more volatile layer be lighter than the other, it is this layer only which boils. On the other hand, perfectly regular results are obtained by following Kundt's method of leading the vapour of one of the boiling liquids into the other;[1] it does not matter which is used as vapour and which as liquid. The proportion between the quantities of the two substances in the vapours is conditioned by the ratio of the two vapour-pressures at the temperature.

If p_1 and p_2 are the vapour-pressures, then the volumes of the two substances in the vapour are in the proportion $p_1 : p_2$, and the quantities by weight are in the ratio $p_1 d_1 \cdot p_2 d_2$, where d_1 and d_2 are the vapour-densities of the two substances; the portions which distil over, q_1 and q_2, follow the law, $q_1 : q_2 = p_1 d_1 : p_2 d_2$. This relation was pointed out for the first time by Gay-Lussac;[2] it was established by Wanklyn,[3] but not for the case to which it is strictly applicable, but for a special instance of the distillation of miscible liquids. Soon afterwards, Berthelot[4] stated the same relation; he also applied the statement to miscible liquids, but at the same time he noted that these liquids did not quite obey the law. Both series of experiments show that the more volatile liquid does not distil over first, under all circumstances; if the vapour-density of the less volatile liquid is considerably greater, the quantity by weight of this liquid which distils over may be greater than that of the more volatile liquid, although the volume of the more volatile liquid in the vapour is greater.

After Pierre and Puchot (see next paragraph) had established the constancy of the proportion of the liquids

[1] *Pogg.* **140**, p. 489 [1870].
[2] *Ann. Chim. Phys.* (2) **49**, p. 396 [1832].
[3] *Proc. R. S.* **12**, p. 534 [1863].
[4] *Compt. rend.* **57**, p. 430 [1863].

distilling over from two partially miscible liquids, A. Naumann [1] applied this result to immiscible liquids; he also pointed out how the process might be used for finding vapour-densities. When the vapour-pressures are known, the relation is $d_1 : d_2 = \frac{q_1}{p_1} \quad \frac{q_2}{p_2}$. The vapour-pressure can be calculated from the difference between the boiling-point of the mixture and that of one constituent, if the vapour-pressure of this constituent (e.g. water) is known at both temperatures. For instance, Naumann got the following results:

	t.	I.	II.	III.
Nitrobenzene . . .	99°	21	19·8	19·4
Ethyl benzoate . . .	99·1	—	15·2	15·9
Naphthalene . . .	98·8	(20)	22	18·7

Column I. contains the vapour-pressure determined directly; column II. contains the vapour-pressure calculated from the difference between the boiling-points, with the aid of the vapour-pressure of water; column III. contains the vapour-pressure calculated by the equation $d_1 : d_2 = \frac{q_1}{p_1} : \frac{q_2}{p_2}$. The values are not very accurate; this is to be expected, as neither does the sum of the vapour-pressures exactly equal the actual vapour-pressure, nor is the assumption of the normal value for the density of water-vapour strictly allowable under these conditions.

5. **Distillation of partially miscible liquids.**—The laws which express the behaviour, on boiling, of liquids which are not miscible one with the other, hold good in part for liquids which are partially miscible. The constituents of the vapours coming from boiling partially miscible liquids bear a constant proportion to one another, and this proportion is independent of the proportion in the liquid, generally speaking as long as two separate layers are maintained. As long as this condition is fulfilled, distillation proceeds at a constant temperature; but, differently from what occurs

[1] *Berichte*, 10, pp. 1421, 1819, 2014, 2099; 11, p. 33 [1877–78].

with immiscible liquids, this temperature is higher than it would be were it dependent only on the sum of the vapour-pressures of the two liquids; in other words, the actual vapour-pressures of such mixtures are smaller than the sums of the vapour-pressures of their constituents at the same temperature. Again, whereas the common boiling-temperature of a mixture of two immiscible liquids is always lower than the boiling-point of the more volatile liquid, the boiling-temperature of two partially miscible liquids may be higher than, or the same as, or lower than, that of the more volatile constituent; the last case is the most common. The occurrence of one or other of the possible cases depends upon the difference between the boiling-points of the constituents of the mixture, and also on the diminution of vapour-pressure caused by the reaction of these constituents. The greater the mutual solubility of the two liquids, the greater may be expected to be the diminution of the common vapour-pressure from the sum of the vapour-pressures of the constituent liquids. For the specific vapour-pressure of a liquid is always decreased by dissolving a foreign substance in the liquid. The magnitude of the decrease depends on the molecular weight of the dissolved substance (this part of the subject will be considered later).

The foregoing relations were observed and fully described by J. Pierre and E. Puchot,[1] in 1872. Experiments were made with mixtures of water with amyl alcohol, butyl alcohol, amyl valerate, butyl iodide, ethyl iodide, butyl butyrate, and propyl propionate. The boiling-point was generally below 100°; in the case of water + amyl valerate the boiling-point was 100° to 100·1°. Constant quantities of the two liquids always distilled over, and neither the proportion nor the temperature changed so long as both liquids were present in the retort. I do not give the authors' actual numbers; they are only approximately correct, and they are not brought into connexion with other properties of the mixtures of liquids.

[1] *Ann. Chim. Phys.* (4), 26, p. 145.

Experiments conducted by D. Konowaloff[1] have thrown more light on the subject of the distillation of partially miscible liquids. It may be asked how the under liquid of the two can exert an influence on the vapour-pressure, as it is hermetically cut off, by the upper layer, from the space containing vapour. Konowaloff has shown that *a solution of liquid* B *saturated with liquid* A *at a specified temperature exerts the same vapour-pressure at this temperature as a solution of* A *saturated with* B. It is therefore immaterial which liquid is the upper and which the under. Konowaloff has given a proof of the foregoing statement which is both theoretical and practical. Some of his experimental results are given here :—

	Ether with Water	*Water with Ether*
	Saturated	Saturated
Temp., 19·8°	vapour pressure = 432·2	vapour-pressure = 430·1
	Ether, Methyl alcohol, and Water	
	Ethereal solution	Aqueous solution
Temp., 15·6°	vapour-pressure = 359·1	vapour-pressure = 358·5
	Ethyl alcohol, Water, and Potash	
	Alcoholic solution	Aqueous solution
Temp., 16·7°	vapour-pressure = 32·35	vapour-pressure = 32·5

The necessity of such a law as that given by Konowaloff can be deduced from first principles. Let fig. 4 represent a ring-shaped hollow space, containing a saturated solution of water in ether at *a*, and a saturated solution of ether in water at *b*, and let *c* contain the vapour of these liquids; then, if the vapour over *a* exerted a different pressure, or were of a different composition, from that over *b*, distillation or diffusion would take place from one side to the other, and this would proceed without cessation, inasmuch as the liquids would continuously

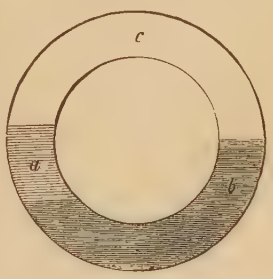


FIG. 4

[1] *Wied. Ann.* **14**, p. 219 [1881].

compensate one another by diffusion. We should have a case of perpetual motion, which is impossible.

As regards the distillation of solutions which have become homogeneous by a large preponderance of one constituent, it is to be noted that the vapours of such solutions at first contain both constituents nearly in the same proportion as in the vapour from heterogeneous mixtures; but as distillation proceeds the proportion of the liquid present in smaller quantity in the solution rapidly falls off, and before long the other liquid remains more or less pure. It matters not whether the liquid present in large quantity is

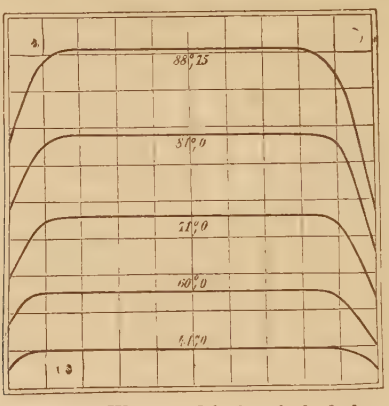


FIG. 5.—Water and isobutyl alcohol

lighter or heavier than the other. The proportions in question are best set forth by representing, as Konowaloff has done, the vapour-pressure at a specified temperature as a function of the proportional quantity, and doing this by means of a curve the abscissæ of which are percentage quantities and the ordinates are pressures. Such curves are given in fig. 5 for mixtures of water and isobutyl alcohol. As the quantity of alcohol increases, the curve quickly rises to a maximum, whereat it remains constant until about 90 per cent. alcohol is present, when it falls to the pressure of pure alcohol. From 10 to 90 per cent. alcohol, the condition of the vapour is independent of that of the liquid; from

this follows, immediately, the constancy of the composition of the distillate, as observed by Pierre and Puchot.

There is a conclusion to be drawn from the results of Konowaloff which he did not himself directly state. The proportional quantities of the two liquids present when one liquid is saturated with the other must be the same as those present when the curve of vapour-pressures changes from a straight to a curved line. The proof of this is found in the equality of the vapour of both saturated solutions, as has been pointed out already.

6. **Distillation of liquids which are miscible in all proportions.**—This operation is of common occurrence in practical chemistry; it is the generally employed method for separating liquids of different boiling-points, the various distillates which come over at different temperatures being collected separately. This separation by 'fractional distillation' depends on the fact that the composition of the vapour coming from a homogeneous mixture of liquids differs from that of the residual liquid in the sense that the vapour contains more of the more volatile than of the less volatile liquid. The more volatile portion of the mixture is concentrated in the distillate by condensing the vapour; and a nearly complete separation of the two constituents may be effected by repeating the operation.

The common vapour-pressure of liquids which are mutually soluble in all proportions does not follow the simple law which holds good for other mixtures, but shows very varying relations which depend upon the reactions of the liquids on one another and on the vapour. The fact may be emphasised at once that *no noticeable action occurs between the vapours themselves.* Bineau [1] found, many years ago, that the vapour-density of aqueous hydrochloric acid, containing 22 per cent. of the acid, which solution distils unchanged, shows that no contraction has occurred between the water-vapour and that of the hydrochloric acid; the two gases mix like indifferent substances without combining.

[1] *Ann. Chim. Phys.* (2) **68**, p. 422 [1838].

By expressing (as was done before) the vapour-pressures as functions of the percentage composition in the form of curves, the change from the typical incompletely miscible liquids (fig. 5) to those that are miscible in all proportions is made evident.

The common vapour-pressure is never equal to the sum of the individual pressures; nor need it lie between this sum and the higher or lower single pressure, although this case occurs frequently, but it may fall considerably beneath the value of the lower single pressure. I give the charac-

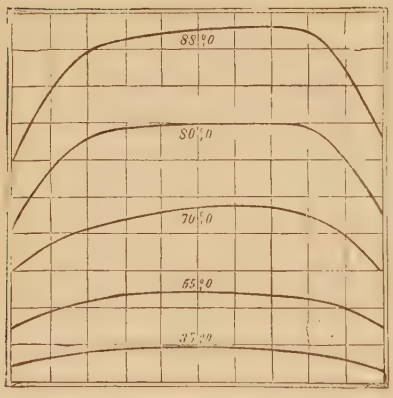


Fig. 6.—Water and propyl alcohol

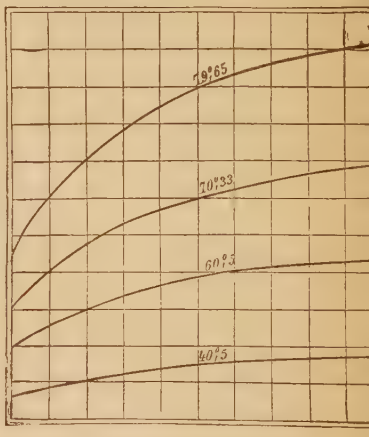


Fig. 7.—Water and ethyl alcohol

teristic curves, from Konowaloff's measurements.[1] The form of the curve for water and propyl alcohol is still similar to that for water and isobutyl alcohol (fig. 5). The two constituents dissolve in one another in all proportions; there cannot, then, be a horizontal part of the curve where the vapour-pressure is independent of the composition, but the common vapour-pressure reaches a maximum between 70 and 80 per cent. of alcohol (fig. 6). No maximum is reached in the case of ethyl alcohol (fig. 7); this property of reaching a maximum disappears also in the case

[1] *Wied. Ann.* **14**, p. 34 [1881].

of methyl alcohol (fig. 8) ; and with formic acid the opposite extreme is reached, the curve changes its convexity, and reaches a minimum at about 70 per cent. of formic acid, i.e. the pressure of the mixture remains lower under all circumstances than that of each constituent, and reaches the smallest value at a certain proportion of the constituents.

Conclusions regarding the behaviour of mixtures on distillation may be drawn from the foregoing considerations. Mixtures belonging to the type of propyl alcohol-water—i.e. those the vapour-pressures of which attain a maximum—will

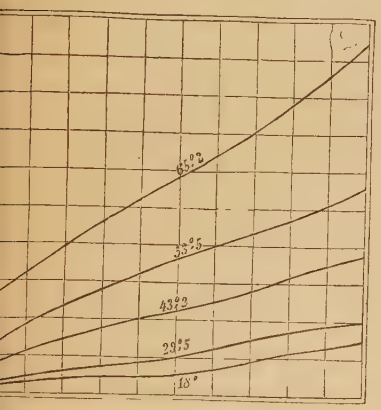


Fig. 8.—Water and methyl alcohol

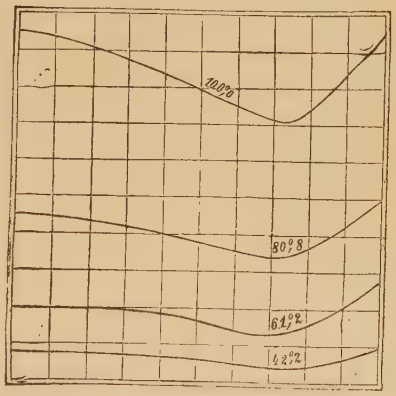


Fig. 9. –Water and formic acid

give off vapour at the beginning of the distillation which contains the constituents nearly in the proportion corresponding with the maximum vapour-pressure, while the composition of the residue will differ from this. By repeated distillation, the final state of affairs will be that a low-boiling distillate with the highest vapour-pressure will be obtained, while that liquid remains which was in excess with respect to the mixture boiling with maximum vapour-pressure. For instance, if a mixture of 50 per cent. propyl alcohol and 50 per cent. water is distilled, a distillate richer in propyl alcohol is obtained, and, after repeated

operations, a low but constant boiling mixture with 75 per cent. alcohol, while water remains. Propyl alcohol of 90 per cent. gives a distillate containing 75 per cent. alcohol, and leaves pure propyl alcohol in the retort. The conditions which prevail may be made plain by keeping before one the fact that every mixture of propyl alcohol and water boils at a lower temperature than either constituent alone, and the mixture with 75 per cent. alcohol has the lowest boiling-point and greatest vapour-pressure; this mixture must be isolated on fractionating.

Mixtures belonging to the ethyl or methyl alcohol-water type suffer, generally speaking, a complete separation when fractionally distilled, because the boiling-points of all possible mixtures lie between those of the constituents. It is, however, much easier to free water from alcohol by distillation than to free alcohol from water, because—and this is indicated by the form of the curve—a small quantity of alcohol in water exerts a much greater effect on the vapour-pressure, and, therefore, on the boiling-point, than a small quantity of water in alcohol.

Finally, formic acid is a case wherein is shown the greatest mutual influence of the constituents; the vapour-pressures of the mixture are all under, and the boiling-points are all above, those of the constituents, and naturally, therefore, a mixture results with the lowest vapour-pressure and the highest boiling-point. On distillation there will always be a tendency for this mixture to remain in the retort, while either water with a little formic acid (in the case of dilute solutions), or nearly pure formic acid, will distil over. In this case, a mixture in the proportion corresponding to the maximum boiling-temperature cannot be separated by distillation; just as in the case of propyl alcohol, a mixture with the minimum boiling-point could not be separated by this means.

7. Aqueous solutions of acids with constant boiling-points.—The fact that mixtures of certain liquids cannot be separated by distillation has been known for long; a careful

investigation of some cases was conducted by Roscoe.[1] Certain aqueous solutions of acids had been regarded as definite hydrates,—$HCl.8H_2O$, $HNO_3.3H_2O$, &c.; but Roscoe showed that neither were the proportions of water and acid those required by any simple atomic formula, nor did the composition remain the same when pressure varied. In the case of nitric acid, the same residue was always obtained, with the maximum boiling-point, whether a more or a less concentrated acid was distilled; but this residue contained 66·7 per cent. HNO_3 if the boiling was conducted at 75 mm. pressure, 68 per cent. HNO_3 at 760 mm., and 68·6 per cent. HNO_3 at 1,200 mm. pressure. Similar numbers were obtained when a dry stream of air was passed through the acid at 60° and 100°; such a process is equivalent to boiling at the same temperature, inasmuch as the partial pressure of the liquid evaporating into the air is equal to the total pressure under which boiling takes place at the temperature in question.

The same kind of phenomenon occurs with hydrochloric acid;[2] only in this case the quantity of acid in the residue decreases, as temperature and pressure increase, from 23·2 per cent. at 50 mm., to 20·24 per cent. at 760 mm., and 18 per cent. at 1,800 mm. pressure. Hydrobromic and hydriodic acids behave similarly. Hydrofluoric acid, on the other hand, like nitric acid, gives a residue which is richer in acid at high than at low temperatures.

These cases agree in all respects with that of formic acid measured by Konowaloff; the aqueous acids with constant boiling-points are mixtures, the vapour-pressure of each of which is at a minimum, and the boiling-point is at a maximum. This relation is shifted in the direction of greater concentration, as pressure increases in the cases of nitric and hydrofluoric acid; in the cases of hydrochloric, hydrobromic, and hydriodic acids it is shifted in the opposite direction. It is possible to suppose the existence

[1] *Annalen*, **116**, p. 203 [1860].

[2] Roscoe and Dittmar: *Annalen*, **112**, p. 327 [1859].

of combinations of liquids in which the minimum vapour-pressure should always occur, independently of the magnitude of the pressure, at the same percentage composition; such combinations would show no differences in the composition of the residues formed at different pressures and different temperatures.

CHAPTER IV

SOLUTIONS OF SOLIDS IN LIQUIDS[1]

1. **Generalities.**—Many solid bodies react with liquids so that both combine to form a homogeneous liquid; in these cases the solid is said to dissolve in the liquid. The quantity of solid dissolved may vary from nothing to a certain limit, after which the solution has no further effect on the solid; when this limit is attained the solution is said to be *saturated*. The limit depends on temperature; when temperature is changed, either some of the dissolved solid separates out, or the liquid dissolves more of the solid. Decreasing temperature is generally accompanied by separation of some of the dissolved body; raising temperature generally produces solution of more solid; there are, however, several exceptions to these rules.

Solutions which are saturated at a specified temperature are obtained, either by agitating the liquid, at this temperature, in contact with the solid, until the latter ceases to be dissolved, or by dissolving more of the solid at another temperature, and then allowing the solution to remain at the specified temperature until separation of the solid ceases. As many substances dissolve so slowly that a long time must elapse before saturation is attained, the first method tends to give results which are too low. On the other hand, inasmuch as solutions may contain more solid, at a given

[1] This chapter is, for the most part, a translation of Chap. VIII. of Book V., entitled *Solubility of Solids*, of Ostwald's *Lehrbuch*. Prof. Ostwald has requested that that chapter should be made use of in the present translation.—*Translator.*

temperature, than they would do under normal conditions, the second method tends to give results which are too high. Solutions which contain more than the normal quantity of solid are called *supersaturated solutions*. When a solid particle of the substance which is held in solution is brought into a supersaturated solution, separation of the dissolved solid proceeds until the normal state of saturation is reached. (See next paragraph.) Regarding solutions with the object of finding the determinate part played by the solid substance, we find the fundamental law to be similar to that which holds good for vapour-pressures. Equilibrium is attained, under definite conditions of temperature and pressure, when the concentration, or specific density, of the solution which is in contact with the solid has attained a certain value; equilibrium does not depend on the relative quantities of the solid and the solution.

The great analogy between solution and evaporation has directed the attention of many investigators to this subject. Before the development of van 't Hoff's theory, one had to be content with the general analogy, without following this up any farther. Since, however, the theory in question has familiarised us with the notion of connecting a definite pressure, viz. the osmotic pressure (see next Chapter), with a dissolved substance, just as a definite pressure accompanies every substance in the state of vapour, the comparison of the two phenomena has become complete, and the accurate application of the general formulæ for vapour-pressures to solutions has been made possible. The development of the theory of van 't Hoff in this direction is due, in great measure, to W. Nernst,[1] who ascribes to a substance in solution a certain *solution-pressure*, in all respects analogous with vapour-pressure.

The molecular conception which we are able to form of the process of solution, and of the existence of a solution-pressure, is connected on one side with the theory of the

[1] *Zeitschr. für physikal. Chemie*, **4**, p. 150 [1889].

mutual solubility of liquids, and on the other side with that of the processes of melting. By reason of their thermal energy, the molecules of a solid tend to separate from one another; this tendency is counteracted by the internal pressure, which acts, normal to the surface, towards the interior, and is existent in solids as well as in liquids. When a solid is brought into contact with a liquid which exerts an action on the molecules situated on the surface of the solid the internal pressure is diminished, and a number of molecules of the solid are removed from the surface and find themselves in the interior of the liquid. This process continues until the number of molecules passing from the liquid to the solid, and remaining there, is equal to the number of molecules leaving the surface of the solid. As the stationary equilibrium thus attained is conditioned, solely, by the processes which occur at the surfaces in contact, it is independent of the relative quantities of the two components.

2. **Supersaturated solutions.**—When the concentration of a homogeneous solution of a solid is brought near to the saturation-point, by evaporation or change of temperature, without the presence of any solid matter, there is, generally speaking, no reason why solid should separate, even if the quantity in solution should exceed that corresponding with saturation. For the establishment of saturation is related, solely, to the equilibrium between solid and dissolved substance; and if the solid is not present, the cause of the production of this definite equilibrium is absent. It is, therefore, possible to prepare a solution of any soluble substance which shall contain more of the solid than corresponds with the conditions of equilibrium when there is no solid matter in contact with the solution. When such a solution comes into contact with a minute particle of the solid, equilibrium is upset, and solid separates, until the quantity in solution corresponds with the specific solution-pressure of the solid. Solutions of this kind are said to be *supersaturated*; their behaviour is analogous in all respects with that of supercooled liquids. The conditions for the production

of supersaturated solutions were well known in the eighteenth century; they were laid down by Lowitz.[1] The older memoirs are gathered together in the fifth edition of Gmelin's *Handbook* (i. 8). The more recent investigators are Loewel,[2] Terreil,[3] Violette,[4] Gernez,[5] de Boisbaudran,[6] Coppet,[7] Jeannel,[8] Dubrunfaut,[9] van Menschbrugge,[10] Reischauer,[11] Baumhauer,[12] Tscherbatscheff,[13] Liversidge,[14] Tomlinson,[15] and others.

The general result of the investigations of these authors is that the only certain cause determining the cessation of the supersaturation of a solution is contact with a crystal of the dissolved substance.

Facts which are of importance as regards the theory of solutions have been noticed during these investigations. Faraday and Ziz found that a supersaturated solution of Glauber's salt $Na_2SO_4.10H_2O$, deposited crystals at a low temperature containing less than 10 molecules of water; Loewel showed the crystals to be $Na_2SO_4.7H_2O$. The quantity of crystals increased on further lowering the temperature, and decreased if temperature were raised; but the solution always remained supersaturated with respect to

[1] *Nov. Comm. Petropol.* xi. 271 [1794]; cited by Frankenheim in *Pogg.* **111**, p. 3 [1860].

[2] *Compt. rend.* **30**, p. 163; **32**, p. 907; **34**, p. 642; **35**, p. 219; **40**, pp. 481, 1169 [1850–55]; *Ann. Chim. Phys.* (3) **29**, p. 62.

[3] *Compt. rend.* **51**, p. 504 [1860].

[4] *Ibid.* **60**, pp. 831, 973 [1865]; **76**, p. 171 [1873].

[5] *Ibid.* **59**, pp, 71. 298, 847; **60**, pp. 833, 1027; **63**, p. 843; **66**, p. 853; **75** p. 1705; **76**, p. 566; **79**, pp. 912, 1332 [1864–74].

[6] *Ibid.* **64**, p. 1249; **65**, p. 111; **66**, p. 497; **68**, p. 1329; **75**, p. 450; **79**, pp. 802, 1074, 1491 [1867–74]; also *Ann. Chim. Phys.* (4) **9**, p. 183; **18**, p. 246.

[7] *Comp. rend.* **74**, p. 328; **76**, p. 434 [1872–73]; also *Ann. Chim. Phys.* (4) **26**, p. 539.

[8] *Compt. rend.* **63**, p. 606; **76**, p. 486 [1866–73]; also *Ann. Chim. Phys.* (4) **6**, p. 160.

[9] *Compt. rend.* **68**, pp. 916, 1218 [1869]. [10] *Ibid.* **76**, pp. 45, 874 [1873].

[11] *Annalen*, **115**, p. 116 [1860].

[12] *J. für prakt. Chemie*, **104**, p. 449 [1868].

[13] *Beiblätter*, 1873. p. 1459. [14] *Proc. R. S.* **20**, p. 497 [1872].

[15] *Phil. Mag.* (4) **40**, p. 295 [1870]; **44**, p. 223 [1872]; also *Proc. R. S.* **20**, p. 41 [1871].

Glauber's salt, and solidified on addition of the smallest fragment of this salt. This is a good example of the fact that the degree of saturation of a solution is dependent on the solid substance with which it is in contact; the solution in question is saturated with regard to $Na_2SO_4 . 7H_2O$, but supersaturated with regard to $Na_2SO_4 . 10H_2O$. Loewel gave a table showing the two orders of saturation.

Crystals isomorphous with the dissolved substance destroy the condition of supersaturation. For instance, different hydrates of nickel sulphate, with different crystalline forms, separate from a supersaturated solution of this salt on addition of different salts of the composition $MSO_4 . xH_2O$. Gernez [1] made use of facts of this kind to separate dextrorotatory or lævorotatory tartrate, at pleasure, from a solution of sodium-ammonium racemate.

These facts all show that the state of supersaturation should not be regarded as abnormal. The properties of supersaturated solutions are by no means sharply separated from those of solutions which are not supersaturated.

One of the earliest experiments on the continuity of the two conditions, which calls for notice, is the observation made by de Coppet,[2] that the influence exerted on the freezing-point of the solvent by the dissolved salt in a supersaturated solution is of the same kind as that exerted by the salt in an unsaturated solution. We are now able to interpret this fact in the sense that no sudden change of the molecular magnitude occurs in the liquid in passing through the point of saturation. That the electrical conductivity suffers no irregular change when the point of saturation is passed has been shown by C. Heim,[3] following measurements made by Beetz [4] for zinc sulphate, and by F. Kohlrausch [5] for sodium sulphate. A similar result was obtained by K. Bindel,[6] who determined the specific gravities, specific

[1] *Compt. rend.* **63**, p. 843 [1867].
[2] *Ann. Chim. Phys.* (4) **23**, p. 366 [1871].
[3] *Wied. Ann.* **27**, p. 643 [1886].
[4] *Pogg.* **117**, p. 1 [1862].
[5] *Wied. Ann.* **6**, p. 28 [1879].
[6] *Wied. Ann.* **40**, p. 370 [1890].

heats, and heats of solution, of supersaturated solutions of salts.

All soluble substances are capable of forming supersaturated solutions; but some substances form these solutions much more readily than others. Glauber's salt, magnesium sulphate, alums, &c., form supersaturated solutions very readily; but it is very difficult to produce supersaturated solutions of nitre or sal ammoniac. The cause of these differences is unknown. Generally speaking, hydrated salts readily produce supersaturated solutions, while salts which crystallise without water do not; but there are exceptions. There is certainly a connexion between the readiness to form these solutions and the readiness of salts to crystallise in large, well-formed crystals. The solutions are supersaturated by evaporation and cooling; solid separates; if the supersaturation is easily effected, the separation of the solid occurs at a few points, and large crystals are formed; but if separation of solid follows slight supersaturation, numerous small crystals are formed, and time is not given for these to grow before diffusion produces a supersaturated solution near them.

3. **Formation of crystals.**—It is certain that the difference between the state of the smallest particles within the liquid in which a crystal forms itself, and the smallest particles within the crystal, is greater than the difference which the change from the liquid to the solid state of necessity implies. Besides the orderly arrangement of the molecules to form a crystalline network, combinations occur, at the moment of solidification, between the molecules of the dissolved substance, and also between these molecules and those of the solvent, and complex structures are thus formed, which did not exist, or existed only to a small extent, in the solution. There are numerous proofs of this. Solutions of a dimorphous substance which have been prepared from the various forms of the substance show no differences; hence the act of solution must break down the special arrangement which conditioned the differences of form.

In the same way identical solutions are obtained from the various hydrates of a salt which crystallises in different forms with different quantities of water, provided the solutions are prepared so as to contain the same quantity of the anhydrous salt. Conversely, compounds of different forms, and different degrees of hydration, are obtained from certain supersaturated solutions by placing a crystal of the desired hydrate in the solution. The question whether hydrated salts exist in solutions in combination with their water of crystallisation is to be answered, in most cases, in the negative. The endeavours of many investigators to find proofs in favour of the existence in solutions of combined water of crystallisation have not led to results which can be received without objection; these endeavours may therefore be passed over.[1]

4. **Influence of pressure on solubility.**—In the opinion of Favre, pressure influences solubility only in so far as it brings about a rise of temperature. But K. Möller [2] showed that change of pressure changes the solubility, independently of change of temperature. In the following data the numbers express parts of salt dissolved in 100 parts of water, at temperature t and pressure p (in atmospheres) :—

Sodium Chloride

	$t=0°$	9°	15°	20°	25°	30°
$p=1$	35·59	35·72	35·70	35·78	35·81	36·01
20	35·79	35·84	35·84	35·82	35·99	36·10
40	35·95		35·87			

Sodium Sulphate

	$t=0°$	15°
$p=1$	4·60	12·76
20	4·74	11·88
30		11·77
40		11·53

[1] A few pages, concerning the growth of crystals, which follow here in the original are omitted.—*Translator.*

[2] *Pogg.* **117**, p. 386 [1862].

Potassium Sulphate

	$t=0°$	15·5°	16·2°
$p=1$	7·31	10·19	10·32
20	7·68	10·43	10·54
30	7·69		

The solubilities of sodium chloride and potassium sulphate increase as pressure increases, but the solubility of sodium sulphate decreases with increase of pressure. The influence of pressure in the case of sodium chloride is smaller the higher the temperature.

Sorby[1] obtained results similar to those of Möller. Sorby went a step farther, and connected the change of solubility accompanying change of pressure with the change of volume which occurs when the salt separates from the solution. If the solution of a salt is accompanied by expansion, and the separation by contraction, as happens with sal ammoniac, then the solubility of the salt is decreased by diminishing the volume by external pressure; on the other hand, if solution is attended with contraction, and separation of salt with expansion, as is generally the case, then the solubility increases as pressure increases. Sorby found that a solution of sal ammoniac saturated at 20° lost 1·045 per cent. of the dissolved salt at a pressure of 164 atmospheres. With salts which cause contraction on solution, he obtained the following results:—

	(1)	(2)	(3)	(4)
Sodium chloride	13·57	97	·407	·419
Copper sulphate	4·83	60	1·91	3·183
Potassium ferricyanide	2·51	86	·288	·395
Potassium sulphate	31·21	63	1·84	2·914
Potassium ferrocyanide	8·90	66	1·64	2·845

Column (1) shows the expansions exhibited by the salts in crystallising from their saturated solutions, the volumes of the crystalline salts being taken as 100; (2) contains the

[1] *Proc. R. S.* 12, p. 538 [1863].

pressures, in atmospheres; (3) gives the percentage increases of solubility (originally dissolved salt=100) at pressures in column (2); in column (4) are found the corresponding increases for a pressure of 100 atmospheres. Sorby adds a column in which is expressed the mechanical force produced by the crystallising of a one per cent. salt-solution; as the process by which the numbers are gained is not clear to me, I have omitted this column.

According to Sorby, the change of solubility by pressure is directly proportional to the change of volume on separation of salt, and to the pressure, and is inversely proportional to the 'mechanical equivalent of the force of crystallisation'; so that the quantity of salt dissolved = $S + \frac{p\,c}{m}$, where p = pressure, c = volume-change on separation of salt, and m is a function of the mechanical equivalent of the force of crystallisation. This formula has not been proved as yet; it does not seem to agree, as regards influence of pressure, with Möller's results; much more experimental work is required before the small differences involved can be determined with accuracy. The decrease in the solubility of sodium sulphate, noticed by Möller, is not in keeping with Sorby's rule, as this salt dissolves in water with contraction of volume.

5. **Investigations of Braun.**[1]—The problem has recently been attacked by F. Braun, with the help of the dynamical theory of heat. I can give here only the most important results. The following equation holds good:—

$$E\,(\lambda - p\,\nu\,\phi) = T\,\eta\,\nu\,\phi;$$

where E = increase of solubility produced by unit-increase of pressure, λ = heat of solution, p = pressure, $\nu\,\phi$ = volume-change brought about by the solution of unit quantity of salt with volume ϕ, T = absolute temperature, η = increase of solubility produced by unit increase of temperature. The

[1] This and several of the succeeding paragraphs have been considerably condensed in the translation. —*Translator.*

quantities are all measured in absolute units. The processes occur with saturated, or nearly saturated, solutions. The equation does not assert that salts which dissolve in their own nearly saturated solutions with contraction always become more soluble at higher pressures, and *vice versâ*, but that whether the change of solution shall be positive or negative depends in part on whether the heat of solution of the salt in the nearly saturated solution is positive or negative. As most salts dissolve with disappearance of heat, the most usual case is that referred to above. The constants for sal ammoniac are as follows : $\lambda = -34{\cdot}4$ cal.,[1] $\phi = {\cdot}6525$, $\eta = {\cdot}0026$, $\mathrm{T} = 273$, $\nu = {\cdot}356$; measuring pressure in atmospheres, E becomes ·000125. Solubility must therefore decrease with rise of pressure ; the decrease will be 1·25 per cent. for 100 atmospheres. An experiment, in which the solution was surrounded with snow to prevent rise of temperature, showed an undoubted separation of crystals of sal ammoniac ; a quantitative estimation was not made, because there was no means at hand for measuring the pressure. The constants for sodium chloride are : $\lambda = -2$ cal., $\phi = {\cdot}4615$, $\eta = {\cdot}000222$, $\mathrm{T} = 273$, $\nu = -{\cdot}177$; assuming λ, η, and ϕ to remain constant, it follows that E is equal to ·000061, and remains nearly constant for pressures up to 500 atmospheres, after which it decreases, and changes its sign at 1,530 atmospheres. Experiments showed an increase of solubility with increasing pressure, and they also pointed to a decrease of solubility at very great pressures. Qualitative agreements were observed between the calculated and the observed results for alum and Glauber's salt.

6. **Influence of temperature on solubility.**—That the solubilities of solids in liquids are affected by temperature has long been known. The first accurate investigation of this influence is found in a memoir by Gay-Lussac.[2] In 1843, Poggiale[3] made determinations of the solubilities of sixteen salts for intervals of 10°, but no general conclusions

[1] Reduced to absolute units by multiplying by $41{\cdot}6 \times 10^6$.

[2] *Ann. Chim. Phys.* (2) **11**. p. 296 [1819]. [3] *Ibid.* (3) **8**, p. 463 [1843].

could be drawn from his results. Measurements were also conducted by Alluard,[1] Mulder,[2] Kremers,[3] and others. A great many determinations of the influence of temperature on solubility have been made in recent years. An investigation, on the lines of that by Gay-Lussac, but using more delicate means for maintaining constant temperatures, has

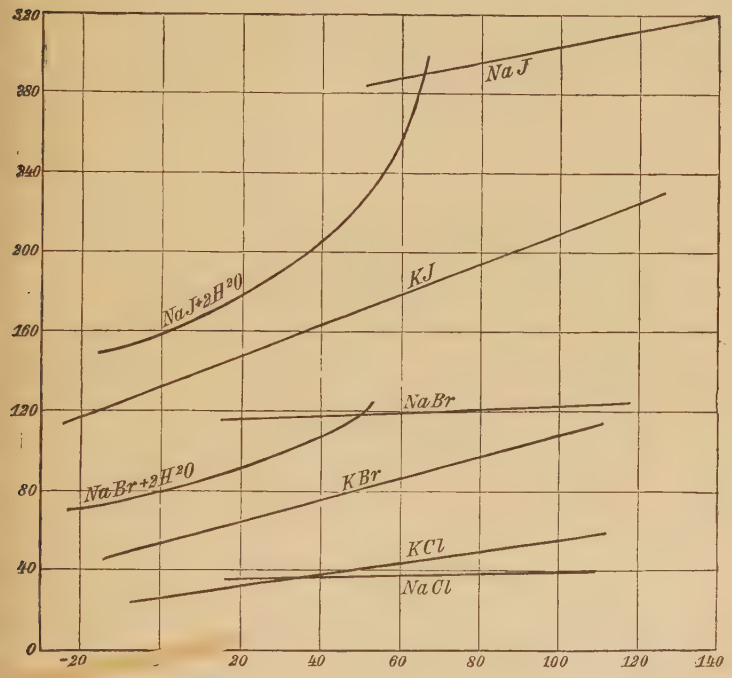


FIG. 10

been made by L. C. de Coppet,[4] with the chlorides, bromides, and iodides of sodium and potassium. The general results are represented in graphic form in fig. 10. It is to be remarked that the solubilities of the six anhydrous salts are represented by straight lines. Either NaBr or NaBr. $2H_2O$

[1] *Compt. rend.* **59**, p. 500 [1864].

[2] *Bijdragen tot de geschiedenis van het scheikundig geboonden Water.* Rotterdam, 1864.

[3] *Pogg.* **97**, p. 1; **99**, p. 25 [1856].

[4] *Ann. Chim. Phys.* (5) **30**, p. 411 [1883].

can be obtained from solutions between 15° and 45°, according as one or other of these is in contact with the solution. Tilden and Shenstone[1] have endeavoured to follow the course of the curves of solubility above 100°. By using a specially arranged tube of gun-metal, heavily plated with silver, they were able to measure solubilities up to 230°.

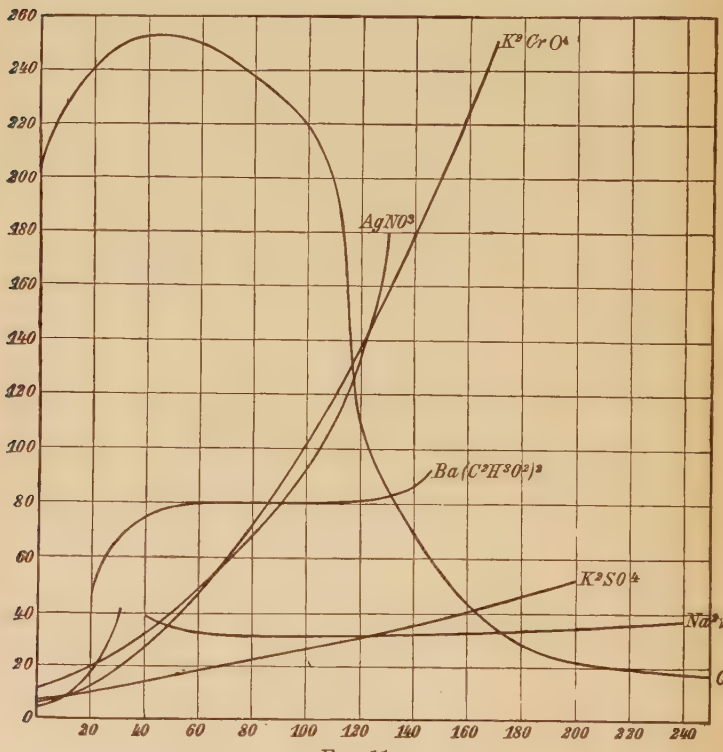


FIG. 11

Sodium sulphate showed a minimum solubility at 120°; above that temperature solubility slowly increased, from 41·95 per cent. at 120°, to 46·4 per cent. at 230°. The solubility of calcium sulphate decreased rapidly as temperature increased; a minimum seemed to be attained at 240°,

[1] *Phil. Trans.* 1884, p. 23.

but this result was uncertain. Some of the results obtained by Tilden and Shenstone are represented graphically in fig. 11. The ordinates for calcium sulphate must be divided by 100; those for silver nitrate must be multiplied by 10. The results led Tilden and Shenstone to conclude that the increases in solubility (not the solubilities themselves) are of the same order as the melting-points of the salts examined.

M. Étard defines solubility, not, as is generally done, as parts of salt in 100 of water, but as parts of salt in 100

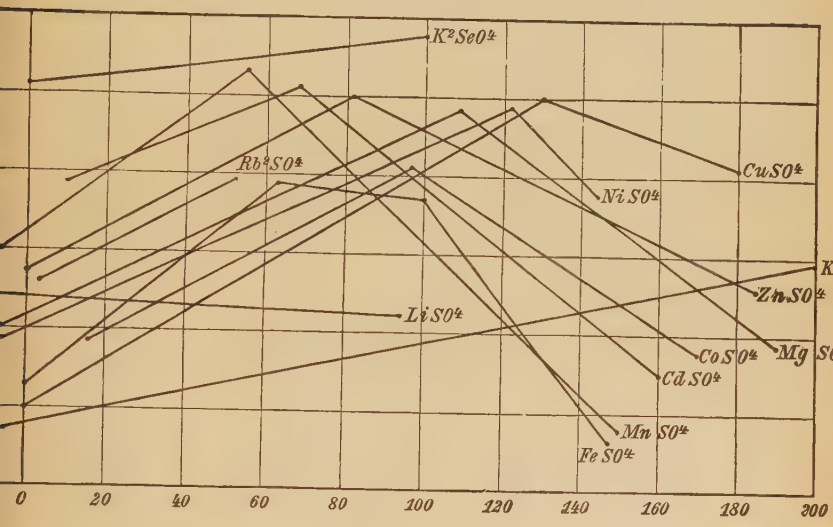


Fig. 12

of the solution; he says that the solubility-curves are either straight lines, or are made up of several straight lines connected by short curved lines.[1] Etard found that the curve for $CuSO_4 . 7H_2O$ consists of three straight lines which meet at 55° and 105°; the salt in contact with the water loses water at 105°, and becomes $CuSO_4 . 3H_2O$. Fig. 12 represents some of Étard's results.[2]

[1] *Compt. rend.* 98. pp. 993, 1276, 1432 [1884].

[2] *Compt. rend.* **104**, p. 1614; **106**, pp. 206, 740 [1887–88]. The relations between solubility and melting-points are considered by Étard in *Compt.*

7. General formulation of influence of temperature on solubility.—The influence of temperature on solubility may be represented algebraically by the ordinary interpolation-equation $1 = a + b\,t + c\,t^2 + d\,t^3 + \ldots$; when the solubility-curve is made up of several parts, a corresponding number of equation must be found. Nordenskjöld [1] sought for a general expression for the relation between temperature and solubility. As solubility generally increases with increasing temperature more rapidly than the temperature increases, Nordenskjöld supposed the increase to be proportional to the quantity of salt, S, already in solution. Hence $d\,\mathrm{S} = \mathrm{S}.\,b\,d\,t$, where t = temperature, and b is a constant; by integration, the expression $\log.\ \mathrm{S} = a + b\,t$ is obtained. This equation is an approximately accurate expression for the solubility; by introducing a second constant an expression is obtained, viz. $\log.\ \mathrm{S} = a + b\,t + c\,t^2$, which represents the experimental results quite accurately.[2] The expression arrived at by Nordenskjöld is, however, only an empirical interpolation-formula.

8. Theory of the solubility-curves.—In seeking for the causes of the influence exerted by temperature on solubility, one is led to consider the similarities between this phenomenon and the vapour-pressures of liquids. As no rational expression has been found for the dependence of vapour-pressure on temperature, so has none been found for the analogous dependence of solubility on temperature. Nevertheless the analogy expressed by Nernst in the notion of 'solution-pressure' may be made use of to deduce certain relations of a general character. The equation frequently used for vapour-pressures, $\frac{d\,p}{d\,\mathrm{T}} = \frac{\rho}{\mathrm{T}\,v}$, may be applied to

rend. **103**, p. 176 [1889]. For other memoirs on solubilities at different temperatures, see Raupenstrauch, *Wien. Akad. Monatber.* **6**, p. 563 [1885]; Miczynski, *ibid.* **7**, p. 255 [1886]; Sedlitzki, *ibid.* **8**, p. 562 [1887]; Keppich, *ibid.* **9**, p. 589 [1888].

[1] *Pogg.* **136**, p. 309 [1869].

[2] The results of experiments are given in the original, and are compared with the calculated numbers.—*Translator.*

solutions; in the original form of the equation p = pressure, T = absolute temperature, ρ = heat of vaporisation, and v = increase of volume in changing to vapour; as applied to solutions, p must be taken to represent osmotic pressure (see next Chapter), or concentration, which is nearly proportional to osmotic pressure, ρ is taken as heat of solution, and v = volume of the solution. As T and v are positive quantities, it follows from the formula that $\frac{dp}{dT}$ and ρ must have the same sign. When heat disappears in the solution of a substance, as heat disappears during evaporation, then the pressure, p, or the concentration proportional thereto, increases with rising temperature; but the solubility of a substance which dissolves with production of heat must decrease as temperature increases. This conclusion has been confirmed simultaneously by Le Chatelier [1] and van 't Hoff.[2] On the other hand, Chacel and Parmentier [3] found that the solubility of calcium butyrate decreases as temperature rises, up to 60°, and that this salt dissolves to form a saturated solution with development of heat; but that although calcium isobutyrate also dissolves with production of a little heat, yet its solubility increases as temperature rises, up to 80°. Le Chatelier [4] showed that the apparent discrepancy was due to experimental errors.

It must be remarked here that the sign of the heat of solution is not to be deduced from the total heat which disappears or is produced on dissolving the salt in water to form a saturated solution, but rather from the quantity of heat which comes into play when the solution passes from the state of saturation at the temperature t to the state of saturation at the temperature $t + dt$; that is, if the expression be allowed, 'the heat of solution in the saturated solution.' As the heat of solution, generally speaking,

[1] *Compt. rend.* **100**, p. 441 [1885].
[2] *Arch. Néerl.* **20**, p. 53 [1886].
[3] *Compt. rend.* **104**, p. 474 [1887].
[4] *Ibid.* **104**, p. 679.

varies much according to the proportion between the dissolved substance and the solvent, it is quite possible that the thermal change accompanying the passage from pure water to saturated solution may have a different sign from that of the thermal change which accompanies the passage from a nearly saturated, to a completely saturated, solution. Such a case has been examined by Reicher and Deventer.[1] The solubility of copper chloride was found to increase as temperature increased, yet the salt dissolved in much water with development of heat. But when a solution was saturated at 48°, was then cooled to 31°, and separation of copper chloride was caused by dropping in a crystal of the salt, a thermometer placed in the solution rose ·6°, although the vessel continually lost heat. As the salt separated from a saturated solution, in this case the 'heat of solution in the saturated solution' was observed; there is, therefore, in this case a disappearance of heat on solution agreeing with the requirement of the curve of solubility. Reicher and Deventer further proved, immediately, that the heat of solution passed through zero as the quantity of water continuously changed.

9. **Further development of the theory.**—In another memoir,[2] Le Chatelier has made wider deductions from the formula already given. Assuming that the gaseous law $pv = \mathrm{R}\,\mathrm{T}$ holds good in the equation $\frac{dp}{d\,\mathrm{T}} = \frac{\rho}{\mathrm{T}v}$, then by substituting $\frac{\mathrm{R}\,\mathrm{T}}{p}$ for v, we have $\frac{dp}{d\,\mathrm{T}} = \frac{\rho p}{\mathrm{R}\,\mathrm{T}^2}$. Differentiating for T, and neglecting the term multiplied by the very small factor $\frac{2}{\mathrm{T}^3}$, the equation is obtained—

$$\frac{d^2 p}{d\,\mathrm{T}^2} = \frac{dp}{d\,\mathrm{T}}\left(\frac{1}{\rho}\cdot\frac{d\rho}{d\,\mathrm{T}} + \frac{\rho}{\mathrm{R}\,\mathrm{T}^2}\right).$$

[1] *Zeitschr. f. physikal. Chemie*, **5**, p. 559 [1890].

[2] *Rech. expér. et théor. sur les Equilib. chim.* [Paris, 1888], p. 138.

From the equation for $\frac{d\,p}{d\,\mathrm{T}}$ it follows that when the temperature is so low that the solubility is very small (the solubility may be said to be proportional to p), then $\frac{d\,p}{d\,\mathrm{T}}$ must be very small; the curve of solubility begins asymptotically to the temperature-axis. As temperature rises the direction of curvature depends upon the sign of $\frac{d^2\,p}{d\,\mathrm{T}^2}$. Now according to experiment $\frac{d\,\rho}{d\,\mathrm{T}}$ is always negative, i.e. less of the heat of solution is taken up, and more is evolved, as temperature

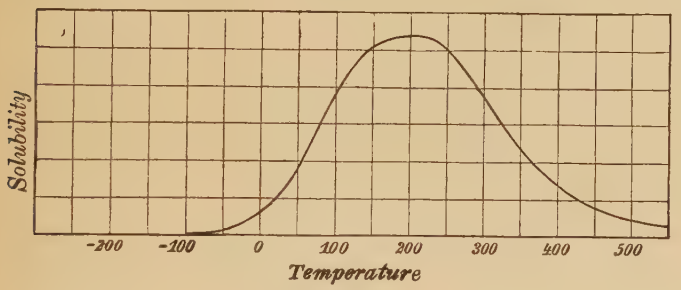


FIG. 13

rises. Both terms in the bracket have, therefore, contrary signs, and $\frac{d^2\,p}{d\,\mathrm{T}^2}$ decreases, passes through zero, and becomes negative. Corresponding to this, the solubility-curve, p, passes upwards convex to the axis of abscissæ, then becomes a straight line for a moment, and then changes its curvature and becomes concave to the axis of the abscissæ. As temperature increases, ρ continues to decrease, and passes through zero, and concurrently also $\frac{d\,p}{d\,\mathrm{T}}$ decreases; solubility reaches a maximum, and then decreases. Following the course of $\frac{d^2\,p}{d\,\mathrm{T}^2}$, here also there is an inflexion-point,

and the solubility-curve runs asymptotically to the temperature-axis.

Figure 13 represents the theoretical curve of solubility. The second part is arrived at by assuming that the development of heat on solution always increases as temperature increases. I do not think this assumption can be accepted without further inquiry, although it holds good, within certain limits, for certain non-volatile substances; yet the second part of the curve will require alteration for certain other, volatile, substances, the heat of solution of which, whether positive or negative, approaches zero as temperature rises.

10. **Quantitative comparison.**—The equation $\frac{dp}{p} = \frac{\rho\, d\,\mathrm{T}}{d\,\mathrm{T}^2}$ or $\frac{dp/p}{d\,\mathrm{T}} = \frac{\rho}{\mathrm{R}\,\mathrm{T}^2}$ may also be written in the form $\frac{d\,l\,p}{d\,\mathrm{T}} = \frac{\rho}{\mathrm{R}\,\mathrm{T}^2}$ where l = the natural logarithm; this form of the equation is better suited for numerical calculations. If the concentrations of a saturated solution are determined at two temperatures, not too far apart, then the difference between their natural logarithms, or the logarithm of their ratio,[1] is taken for $d\,l\,p$, and the corresponding temperature-difference enters the equation as $d\,\mathrm{T}$; T is the mean temperature of experiment, and R is equal to 2 cals. in thermal measure, in which measure ρ also is expressed. The data are thus given for calculating ρ, the heat of solution, from the solubility-curve. It is to be noted that the constants R have not their usual values in solutions of salts, which, generally speaking, are electrolytes, but must be multiplied by van 't Hoff's factor i (see Chapter IX.). The earliest calculations were made by van 't Hoff,[2] who gave the following table (the values of the calories in the two last columns are divided by 1000) :—

[1] It does not matter in what units the concentrations or pressures are measured, as it is only the ratio that enters into the calculation.

[2] *Arch. Néerl.* 20, p. 55.

	Temperature		Solubilities		i	ρ calculated	ρ observed
Oxalic acid	0°	10°	5·2	8·0	1·25	8·2	8·5
Potassium binoxalate	0	10	2·2	3·1	1·84	9·8	9·6
Succinic acid	0	8·5	2·88	4·22	1	6·9	6·7
Salicylic acid	12·5	81	·16	2·44	·93	8·4	8·5
Benzoic acid	4·5	75	·182	2·193	·93	6·3	6·5
Potassium bichromate	0	10	4·6	7·4	2·36	17·3	17·0
Amylic alcohol	0	18	4·23	2·99	·93	−3·1	−2·8
Aniline	16	55	3·11	3·58	·83	·6	·1
Phenol	1	45	7·12	10·2	·84	1·2	2·1
Baryta	0	10	1·5	2·22	2·69	16·3	15·2
Lime	15·6	54·4	·129	·103	2·59	−2·8	−2·8
Alum	0	9·38	3·0	4·05	4·45	21·9	20·2
Mannite	17·5	23	15·8	18·5	·97	4·8	4·6
Mercuric chloride	10	50	6·57	11·84	1·11	3	3
Potassium chlorate	0	15·4	3·3	6·03	1·78	11	10
Boric acid	0	12	1·95	2·92	1·11	5·8	5·6
Borax	0	10	2·83	4·65	3·57	27·4	25·8

These calculations are only of a provisional nature, as the observations on which they are based differed considerably. Nevertheless, a comparison of the last column with that preceding it, shows that the equation expresses the solubilities quantitatively as well as qualitatively.

It should be noted that the heats of solution can be calculated from the course of the curve of solubility, but that the curve itself cannot be deduced from the heats of solution, inasmuch as the equation gives only the direction of the curve, but does not give any actual value for the solubility. If the equation $\frac{d\,l\,p}{d\,T} = \frac{\rho}{R\,T^2}$ is integrated, the result is $l\,p = \int \frac{\rho}{R\,T^2} +$ const., or, if ρ is regarded as independent of temperature, $l\,p = -\frac{\rho}{R\,T} +$ const.; the integration-constant determines the numerical value of the solubility, but this constant cannot be found by the help of the equation.

The direction in which a general expression for the solubility as a function of the temperature is to be sought for, is made evident from the foregoing considerations :—

the heat of solution must be regarded as a function of the temperature, e.g. $\rho = \rho_0 + \beta t$; the equation must be altered to correspond with this, then integrated, and then compared with the experimental results. In doing this, it must be borne in mind that the factor i enters into the equation for electrolytes, and that this factor also is a function of the temperature.

11. **Compound solubility-curves.**—It appears from the preceding paragraphs that the solubility-curve of a substance must have a regular course; the curvature may alter gradually, but there can be no sudden change of direction as long as the dissolving substance undergoes no change of state whereby its heat of solution, ρ, suffers sudden change. Experimental results, however, seem to go against this conclusion. Since Gay-Lussac's measurements, it is known that the solubility-curve of sodium sulphate suddenly changes its direction at 33°; up to that point solubility increases, but after that point it decreases as temperature rises. It was supposed, formerly, that the state of the dissolved salt underwent a sudden change at 33°, that the salt with $10H_2O$ existed in solution below this temperature, but a salt with less water, or the anhydrous salt, existed above this temperature. This supposition is not, however, borne out, but is rather contradicted, by the facts; for all the properties of a solution of sodium sulphate—such as vapour-pressure, expansion, refractive power, electric conductivity—change in an exactly similar way in passing through the temperature in question, whereas some irregularities would certainly be noticeable did the condition of the salt in solution undergo a sudden change. The only feasible supposition is that the condition of the undissolved salt, which modifies the solubility in a definite way, suffers a sudden change at 33°. The condition of the undissolved salt was overlooked for a long time; but the circumstance is of great importance, for when the solution is saturated there is an equilibrium between the solid salt and the solution in contact therewith, and this equilibrium must be determined by both these

factors. Inasmuch as no sudden change takes place in the solution, such a change must be sought in the solid substance, where indeed it is found. The equilibrium of a saturated solution of sodium sulphate below 33° has reference to ordinary Glauber's salt, $Na_2SO_4 . 10H_2O$. But at 33° this salt melts partially, and changes into a saturated solution and the anhydrous salt Na_2SO_4. An entirely new curve of solubility, that of the anhydrous salt, begins at 33°. This curve must have a point in common with that of the ordinary Glauber's salt, at the temperature whereat both salts exist side by side; but from this point onwards the curve of the anhydrous salt is quite independent of that of the other salt.

In the case of Glauber's salt, we have not, therefore, to do with one solubility-curve, but with two curves, which are independent of one another to a certain temperature. The same thing happens in all cases where irregularities occur in the course of the solubility-curve; and, conversely, irregularities are to be expected in the curves of all substances which undergo sudden changes in the solid form.

12. **Behaviour of thorium sulphate.**—Thorium sulphate is a very good example of the connexion between the solubility of a salt and the composition of the undissolved portion of the salt. This case has been investigated by Bakhuis Roozeboom.[1] The salt $Th(SO_4)_2 . 9H_2O$ forms a stable solution at low temperatures; the solubility increases with increasing temperature; the curve A B C of fig. 14 represents this connexion; it can be followed to about 55°. At higher temperatures a flocculent salt, $Th(SO_4)_2 . 4H_2O$, separates; this salt dissolves in water with production of heat; the solubility-curve of this salt from 18° to 95° is represented by E D in fig. 14. The two curves intersect at 43°; at this temperature both hydrates exist together. Two saturated solutions of thorium sulphate, then, exist between 18° and 55°; one has reference to the salt with $9H_2O$, the other to the salt with $4H_2O$. The first changes into the

[1] *Zeitschr. f. physikal. Chemie*, 5, p. 198 [1890].

second between 43° and 55°, with separation of the salt with $4H_2O$; the second changes into the first between 18° and 43°, with separation of the salt with $9H_2O$. Both these changes do not take place necessarily; they occur the more readily the further temperature is removed from 43°, which is the point of equilibrium. It is very noteworthy that the salt $Th(SO_4)_2 . 9H_2O$ can exist in contact with the solution, although the conditions are present for at

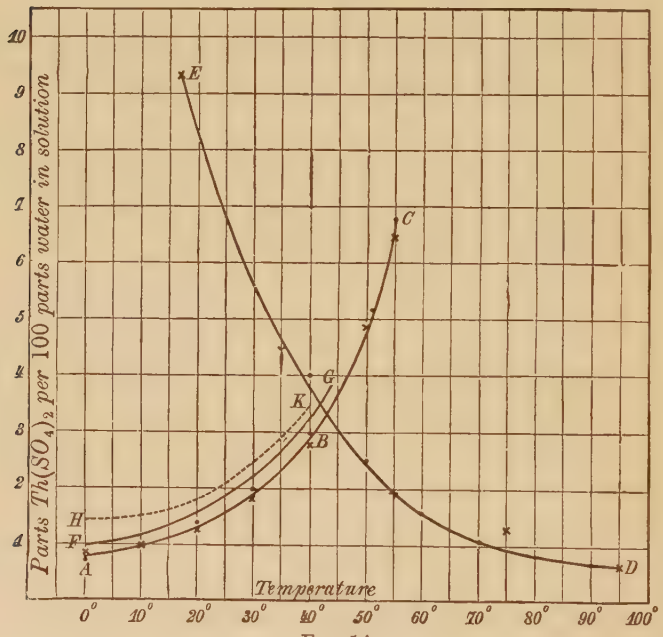


FIG. 14

least a partial melting to form a saturated solution [which contains about $700H_2O$ for one $Th(SO_4)_2$], and at the same time to produce the salt with $4H_2O$. There are many other solubility-curves besides the two which have been described. The curve for the anhydrous salt could not be determined, as the salt with $9H_2O$ separated very easily from the solution. The curve FG represents the solubility of the salt $Th(SO_4)_2 . 8H_2O$; this curve

was followed to 60°. Another salt with $6H_2O$ was obtained; the solubility-curve is represented by H K. Finally there is a salt with $2H_2O$, which separates from the solution at about 100°. Thorium sulphate differs from most other salts in the remarkable stability of its hydrates; this stability made it possible to trace the different curves separately. It must be remembered that all the solutions are supersaturated, below 43° as regards the salt with $9H_2O$, and above 43° as regards the salt with $4H_2O$; crystallisation can always be determined by throwing in a small quantity of one or other of these salts. The solutions are extremely stable in the neighbourhood of the point of equilibrium.[1]

13. **Influence of melting on solubility.**—Gay-Lussac was the first to examine the effect on the solubility of a substance produced by the change from the solid to the liquid state.[2] He failed to detect any sudden increase of solubility. This result may be shown to be necessary. The solid and the liquid substance can coexist in any proportion at the melting-point; if we suppose each to be in equilibrium with its own saturated solution, the contents of the two solutions must be equal; for if this is not so, diffusion will take place until equality results; and hence, at a constant temperature, increase of one portion will occur at the cost of the other, with an accompanying spontaneous formation of differences of temperature in a system which was originally all at the same temperature; but this is against the second law of thermo-dynamics. The reasoning is the same as that which is used to show the necessity for an equal vapour-pressure over a solid and a liquid substance. The analogy between solution and evaporation may be carried farther. It is known that the curves of vapour-pressure of a solid and a liquid substance must meet at an angle the magnitude of which is determined by the heat of

[1] Bakhuis Roozeboom has made a very thorough and careful examination of the hydrates of calcium chloride, similar to that described for thorium sulphate.—*Rec. Trav. Pays-Bas*, **8**, p. 1 [1889]; abstract in *Zeitschr. f. physikal. Chemie*, **4**, 31 [1889].

[2] *Ann. Chim. Phys.* (2) **70**, p. 423 [1839].

fusion. From this it follows that, if the solubilities of the solid and liquid portions of a substance must be the same at the melting-point, the solubility-curves must meet at an angle which is dependent on the heat of fusion. This conclusion has been tested and confirmed by J. Walker.[1]

From the equation $\frac{dp}{dT} = \frac{\rho}{Tv}$, using the equation for gases $p\,v = R\,T$, which holds good also for solutions, there is deduced the equation $\frac{dp}{p} = \frac{\rho}{R\,T^2}\,dT$; and by integration we have

$$T\,lp = -\frac{\rho}{R} + \left(l\,p_0 + \frac{\rho}{R\,T_0}\right) T$$

This equation holds for solid substances. A similar equation is valid for melted substances, only the heat of solution must be increased by the heat of fusion, λ. The equation becomes

$$T\,lp' = -\frac{\rho + \lambda}{R} + \left(l\,p_0 + \frac{\rho + \lambda}{R\,T_0}\right) T$$

The values of $T\,lp$ are represented as ordinates in a system of co-ordinates, and the values of T as abscissæ. If $l\,p_0 + \frac{\rho}{R\,T_0} = a$, and $l\,p_0 + \frac{\rho + \lambda}{R\,T_0} = a'$; then $\lambda = R\,T_0\,(a' - a)$. Taking λ as molecular heat of fusion, $R = 2$ cal., and the equation becomes

$$\lambda = 2\,T_0\,(a' - a).$$

Values are found for a and a' by experiment; and the value of λ is calculated therefrom.

Walker carried out an investigation with para-toluidine dissolved in water; the melting-point of the substance under water was 44·2°. Fig. 15 represents the results. The value for λ calculated from these results is 4,761, or 44·5 cal. per gram. The directly observed number is 39 cal.

[1] *Zeitschr. f. physikal. Chemie*, 5, p. 192 [1890].

per gram. The difference is certainly not a small one; but a small error in determining the course of the curves has a great influence on the value of λ, because of the smallness of the angle between the two curves of solubility. The calculation is only approximate, as no attention was paid to the circumstance that liquid toluidine retains water under its saturated solution, and this taking up of water is accompanied by some thermal reaction.

A second series of measurements of water in ethereal solution gave a remarkable result. The heat of fusion of

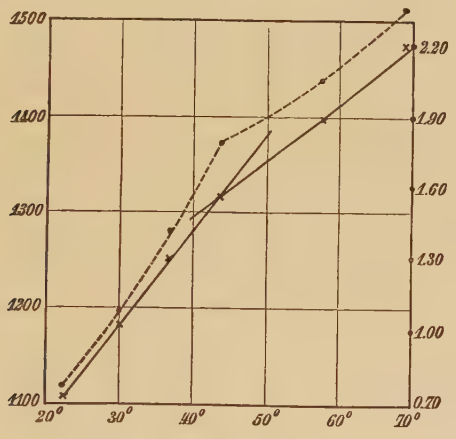


FIG. 15

water was calculated to be 154 cal., whereas it is known to be 80 cal. The larger number was obtained by supposing that the molecular weight of water dissolved in ether is 18; if it is supposed that the molecule of water in solution in the ether is represented by the formula $H_4O_2 = 36$, the heat of fusion becomes 77 cal., which is as near as can be expected to the true value, 80 cal. This result agrees with that obtained by Eykman (see Chap. VIII. par. 13).

14. **Influence of the nature of the solvent and of the dissolved substance.**—No satisfactory answer has yet been found to the inquiry concerning the dependence of solubility

on the chemical nature of the dissolved substance, as well as on the nature of the solvent.

It may be said, in general terms, that solubility is determined to some extent by the chemical analogies both of the dissolved substance and the solvent.

Most of the compounds which belong to the water-type, and especially the hydroxyl compounds, dissolve more or less readily in water. The alcohols and organic acids, for instance, are generally soluble in water, the solubility decreasing as the quantity of carbon in the compounds increases. The fatty acids, as far as the fourth member of the series, are miscible with water in all proportions, but the higher members show increasingly smaller solubilities. The same holds for the corresponding alcohols. The aromatic acids and alcohols are much less soluble in water; they contain, relatively, more carbon. While benzene, C_6H_6, is insoluble, phenol, $C_6H_5.OH$, dissolves in water to about 2 per cent.; hydroquinone and its isomerides, $C_6H_4(OH)_2$, dissolve fairly freely; and pyrogallol, $C_6H_3(OH)_3$, dissolves in almost all proportions in water. Almost all alcohols seem to be soluble in common alcohol; and all organic acids, apparently without exception, are soluble in acetic acid. All hydrocarbons dissolve, more or less, in benzene. Only such general statements as the foregoing can be made concerning the relations under consideration; these relations have scarcely been studied quantitatively.

The solubilities of many salts in water have been measured; but only a few general statements can be made; quantitative laws have not yet been arrived at. The solubilities of analogous compounds of similar elements often vary, either directly or indirectly, as the atomic weights of the elements; for instance, the solubilities of the sulphates, chlorides, and nitrates of barium, strontium, calcium, and magnesium, increase in the order given, but the solubilities of the hydroxides decrease: the solubilities of the chloride, bromide, and iodide, of potassium decrease; but those of the same salts of lead increase, as the atomic weight of the halogen

increases. Kremers[1] made numerous measurements, but he could not deduce any general laws.

The reason why no exact relations have been traced between the nature of the dissolved substance, the nature of the solvent, and the solubility, is to be found in the relative character of the property of solubility. This property, as has been seen already, depends not only on the chemical nature of the dissolved substance, and on that of the solvent, but it is also conditioned by the constitution of the undissolved portion of the solid in contact with the solvent. If the constitution of the solid should change with change of temperature, e.g. if the amount of the water of crystallisation should vary, then the solubility varies also; and the solubility is no longer comparable with that before the change of constitution, nor is it comparable with that of other substances which may be analogous with the substance under examination in all other respects.

There is also another circumstance which must be taken into account in considering aqueous solutions of salts. The condition of a salt in aqueous solution is not at all like that of an indifferent substance; the properties of salt solutions depart very much from the simple conditions which hold with indifferent substances; the molecular condition of the dissolved salt must be regarded as that of a more or less dissociated substance (see Chap. VII.). This dissociation is dependent on concentration and temperature; hence in dealing with solutions of salts, we have to do with very complex relations which cannot be elucidated without making determinations of the other properties of the solutions.

15. **Indifferent substances.**—Much more simple relations are to be looked for in solutions of indifferent substances than in solutions of salts; such simple relations have been observed by Carnelley and A. Thomson.[2] They give the following rules:—the most fusible of a group

[1] *Pogg.* **92**, p. 497; **94**, pp. 87, 255 [1854–55].
[2] *C. S. Journal*, **53**, p. 782

of isomeric organic compounds is also the most soluble, and this independently of the nature of the solution; the solubilities of the salts of a group of isomeric acids, as well as the solubilities of the acids themselves, are in the same order as the melting-points of the acids; the ratio of the solubilities of two isomerides is nearly independent of the nature of the solvent.[1] Measurements of the solubilities of some members of homologous series of carbon acids are given by L. Henry.[2]

16. **Volume-relations of solutions.**—The solution of a solid in a liquid is accompanied, in most cases, with contraction of volume; the volume of the solution, in most cases, is smaller than the sum of the volumes of the solid and the solvent at the same temperature. The measurements made refer to aqueous solutions. The contraction is dependent on the proportion between solid and solvent, and increases as the quantity of solvent used increases for the same quantity of solid. The increase is the less, for equal increments of solvent, the greater is the quantity of solvent already present, so that the contraction approaches a maximum asymptotically. Michel and Krafft[3] supposed that no contraction occurred on diluting solutions of salts; this was disproved by Kremers.[4] It appears, from the measurements of Kremers, that, in many cases, the specific gravities of solutions of equivalent quantities of similar salts are the greater, the greater the molecular weight of the salt. No general relation could be traced between the magnitude of the contractions and the composition of the dissolved salts.[5]

[1] For measurements, and for a tabular statement of the exceptions from each rule, see the original memoir.

[2] *Compt. rend.* **99**, p. 1157 [1884].

[3] *Ann. Phys. Chim.* (3) **41**, p. 471 [1854].

[4] *Pogg.* **95**, p. 110; **96**, p. 39 [1855].

[5] For other measurements, see Schiff, *Annalen*, **109**, p. 325; **113**, p. 349 [1859–6]; also Favre and Valson, *Compt. rend.* **73** to **77** [1872–73]. A paragraph is devoted in the original to a warning against the unwarrantable use of interpolation-formulæ: the following sentences occur: 'When the rational connexion between two phenomena, which mutually con-

17. Solubilities of mixtures.—The phenomena shown by the solutions of mixtures are very complex. Kopp[1] was the first to institute systematic investigations; he examined salts which could not mutually decompose one another, and contained either the same metal or the same acid. For such pairs of salts as nitrate and sulphate of potassium, nitrate and chloride of potassium, sulphate and chloride of potassium, Kopp found that the quantity of each salt dissolved by water from the mixture was always less than that which the water would have dissolved had it acted on that salt alone. Kopp also found that the quantities of the salts dissolved were not in the ratios of their individual solubilities, but that proportionally more of the more soluble constituent was dissolved.

The behaviour of pairs of salts of the same acid was more regular. In these cases, the more soluble salt generally dissolved as in pure water, but the quantity of the other salt which dissolved could not be calculated from its specific solubility.

The subject was more fully examined by C. T. B. Karsten.[2] Karsten distinguished three cases in the behaviour of saturated salt-solutions towards other salts, not taking into account those cases in which chemical changes occurred between the constituents. (I.) When the salt A is treated with a saturated solution of B, the salt B separates in the solid form, and conversely; the same final condition is reached in both cases, and A and B remain dissolved in less quantity than they would dissolve in pure water. (II.)

dition one another, is unknown, the relation between them may nevertheless be expressed, to any degree of approximation, by a suitable, but in other respects arbitrary, equation. Such an equation has none of the properties of a natural law; it is only an algebraic device, based on the assumption that both the phenomena in question proceed continuously, for aiding the calculation of the connected values for such points as are within the scope of the inquiry, but for which direct measurements have not been obtained.'

[1] *Annalen*, **34**, p. 260 [1840]. For older observations, see Vauquelin, *Ann. Chim. Phys.* **13**, p. 86 [1792]; Longchamp, *Ibid.* **9**, p. 5 [1818].

[2] *Abhand. der Berlin. Akad.* 1841.

The salt A causes the separation of solid salt from the saturated solution of B, but A itself dissolves to the same extent as it would do in pure water. Hence no separation of solid occurs when B is added to a saturated solution of A, but a certain quantity of B dissolves, and this quantity is less than that which dissolves in pure water. In this case, as in the first case, identical results are obtained whether one starts with a saturated solution of A or of B, or whether one treats a mixture of both salts with so much water that a portion of each remains undissolved. (III.) Neither A nor B causes a separation of the other from its saturated solution, but the saturated solution of either dissolves some of the other salt when shaken with it. Hence the same solutions are not obtained by treating the two saturated solutions each with the other salt, but the same solution results when excessive quantities of both salts are treated with water.

Karsten thinks that, in every case, provided both salts are present in excess or in sufficient quantity, the solution contains the two salts in determinate quantities which are independent of the proportion of the salts in the part which remains undissolved. Hauer,[1] however, has shown that if one salt is added in sufficient excess it is sometimes able to displace the other, wholly or almost wholly, from its solution. This observation was made with isomorphous salts; Hauer regarded isomorphism as a necessary condition.

18. **Investigations of Rüdorff.**—In 1873, Rüdorff[2] examined the solubilities of mixtures of salts, with especial reference to the question whether a solution of definite contents can be obtained independently of an excess of one or the other salt. He found that the composition of saturated solutions of certain mixtures prepared by agitation, was not altered by dissolving therein an excess of either salt at a higher temperature, and then allowing

[1] *J. für prakt. Chemie*, **93**, p. 137; **103**, p. 114 [1866–68].
[2] *Pogg.* **148**, pp. 456, 555.

the solution to stand at the temperature at which it was made originally. Other mixtures behaved differently. The following pairs of salts form solutions of constant composition; the quantity of each salt dissolved by 100 parts of water, at the temperature specified, is given in the table. The columns headed *a* and *b* give the quantities of the salts which dissolve in pure water at the temperature of observation; generally these quantities are greater than those present in the solution of the two salts.

Exp.	Salts	Parts dissolved by 100 parts water	Temp.	*a*	*b*
1	$NH_4Cl + NH_4NO_3$	29·1 + 173·8	19·5°	37·0	183·0
2	$KI + KCl$	133·2 + 10·4	21·5°	146·2	35·2
3	$KCl + NH_4Cl$	19·1 + 30·4	22°	35·3	38·0
4	$KCl + NaCl$	15·7 + 29·9	18·8°	34·3	36·0
5	$NaCl + NH_4Cl$	23·9 + 22·9	18·7°	36·4	22·0
6	$NaNO_3 + NH_4NO_3$	77·1 + 162·9	16°	84·7	106·0
7	$KNO_3 + KCl$	19·1 + 35·2	20°	—	—
8	$NaNO_3 + NaCl$	56·8 + 24·6	20°	—	—
9	$(NH_4)_2SO_4 + NH_4Cl$	46·5 + 26·8	21·5°	—	—
10	$KNO_3 + Pb(NO_3)_2$	67·1 + 119·6	21·2°	32·6	53·3
11	$NH_4Cl + BaCl_2$	33·8 + 11·6	20°	37·2	35·7
12	$Na_2SO_4 + CuSO_4$	15·9 + 20·7	15°	13·4	20·5
13	$NaCl + CuCl_2$	16·0 + 72·6	15°	—	—

Either of the salts in any one of the following pairs of salts causes separation of the other salt from its solution :—

KNO_3	and NH_4NO_3	$(NH_4)_2SO_4$	and $CuSO_4$
$Ba(NO_3)_2$	„ $Pb(NO_3)_2$	K_2SO_4	„ $CuSO_4$
$Sr(NO_3)_2$	„ $Pb(NO_3)_2$	$(NH_4)_2SO_4$	„ $ZnSO_4$
NH_4Cl	„ $CuCl_2$	$CuSO_4$	„ $FeSO_4$
		$MgSO_4$	„ $ZnSO_4$

It is, therefore, not only isomorphous salts, as Hauer supposed, but also those which form double compounds, that mutually drive out one another from solutions.[1]

19. **General consideration of the common solubility of several substances.**—The analogy between solution and eva-

[1] For more recent researches by Rüdorff, on the same lines and with similar results, *v. Wied. Ann.* **25**, p. 626 [1885]; *v.* also Engel, *Compt. rend.* **102**, p. 113 [1886].

poration helps us to gain a clearer insight into the conditions which regulate the simultaneous solution of several substances. Three cases have been distinguished in the evaporation of mixed liquids (Chap. III.); these cases depend on the degree of influence which the constituents of the liquid exert on one another. Liquids which do not mutually dissolve possess the same vapour-pressures when mixed as when separate; the vapour-pressure of the mixture is the sum of the vapour-pressures of the constituents. The analogous case for solutions is that where the two solids exert no action on one another. In this case, the solution becomes saturated with reference to each constituent, and the proportion between solid and solution does not affect the equilibrium of saturation. Neither is the proportion between the two solids of importance, provided that enough of each is present to saturate the liquid. The first class of salts examined by Rüdorff corresponds, to some extent, to this case; the salts do not form double compounds, nor do they crystallise together isomorphously. Most of the salts examined are very soluble in water, and their saturated solutions exhibit very considerable osmotic pressures. In conformity with this, the solubilities of the individual salts are not retained exactly in the mixture, but are generally smaller; a similar thing happens in the analogous case of evaporation. Other actions also come into play with salts; the simpler case of indifferent substances has not yet been examined.

The second case, for liquids, is that of partial mutual solution. There is no exactly corresponding case for solutions of solid salts; but a certain degree of similarity exists when the two salts are capable of crystallising together as a double salt. Several cases are then possible. As the formation of a double salt does not necessarily always follow, a solution may be formed at first which is saturated as regards both salts; no satisfactory example of this case has been examined yet. When the double salt has been formed, then either the salt A, or the other salt B, may be

present in excess: two states of equilibrium may result; one in which the double salt is in equilibrium with the salt A, and the other in which it is in equilibrium with the salt B. This is the case usually observed. On adding an excess of B to the saturated solution of A, the double salt separates; this double salt must be, always and necessarily, less soluble than either of its constituents. The solution becomes poorer in A, and it is customary to say that A is forced out of solution; although it is not A, as such, that separates, but a double salt of which A is a constituent. If there is sufficient of B present, a solution soon results, which is saturated both as regards the double salt and B, and *which is not changed on addition of more of* B—a point which was overlooked by Rüdorff. In this case the separation from solution of either constituent cannot, therefore, be complete. This conclusion was verified by measurements made by me in 1884 (but not published), with ammonium sulphate and copper sulphate; on gradually adding small quantities of ammonium sulphate to a saturated solution of copper sulphate, the solution at first became poorer in the copper salt, but a limiting state was reached which was not changed by further addition of ammonium sulphate. If B is not present in such quantity that some of it remains in the solid form along with the double salt, then the solution which is formed is to be looked on as a saturated solution of the double salt in an unsaturated solution of B. Under these conditions the solubility of the double salt is greater than it is in the saturated solution of B, and this solubility varies inversely with the quantity of B. This is the case to which most of Rüdorff's investigations apply, and which led him to conclude that saturated solutions could not generally be obtained under the conditions of his experiments. The same considerations hold good when A is in excess. A fourth state of saturation is possible wherein the equilibrium is between the double salt and the solution only. A case of this kind was examined by Gay-Lussac in his investigation of the solubility of alum. The phenomena become much

more complex when the formation of several double salts from two constituents is possible.[1]

The third case of mixed liquids is that where both parts are mutually miscible in all proportions; the vapour-pressures vary continually, but not, as a rule, regularly, between the limiting values. The corresponding case for solutions of two salts is that wherein the salts are able to crystallise together in all proportions; this usually happens only when the salts are isomorphous, but such salts have not always this power. The composition of the saturated solution changes continuously with the composition of the isomorphous mixture; by adding successive quantities of B, it is possible to displace the salt A entirely from the solution. In principle, an infinite quantity of B is required; but to displace so much of A that this salt can no longer be detected by analytical methods, only a finite quantity of the isomorphous salt is needed.

All the foregoing considerations may be followed without using the analogy between the phenomena in question and the evaporation of liquids; it is only necessary to regard the equilibrium between the solution and the solid substance as dependent on, and varying with, the composition of the solid. The conditions of saturation do not vary, or vary discontinuously, or vary continuously, according as the composition of the solid is unchanged, or varies by leaps, or varies continuously. The advantage of using the analogy with evaporating mixtures of liquids is that both sets of phenomena are cases of equilibrium of heterogenous systems which can be expressed by corresponding general laws.

20. **Influence of acids on the solubilities of their salts.**—The researches of R. Engel[2] on this subject belong to the domain we are now considering. Measurements were made with hydrochloric acid and chlorides; they led to the

[1] These cases are considered by the author in that part of his work which treats of chemical equilibrium in heterogeneous systems.—*Translator.*

[2] *Compt. rend.* **102**, p. 619; **104**, p. 433 [1886–87].

approximately accurate statement that the amount of chloride displaced from a saturated solution corresponds with the chlorine in the acid which is added; the total chlorine, or the sum of the equivalents of chloride and hydrochloric acid, remains therefore nearly constant when the quantity of hydrochloric acid varies. Thus :—

Barium Chloride	Hydrochloric Acid	Sum of the Equivalents
29·45	0	29·45
27·8	1·1	28·9
26·08	2·8	28·88
23·4	5·0	28·4
14·0	14·36	28·36
10·2	18·78	28·98
6·67	22·75	28·42
2·74	32·0	34·74
0·29	50·5	50·79

The numbers represent milligram-equivalents in 10 c.c. of the solution. The experiments were conducted at 0°; each number is the mean of three independent observations. The law holds good approximately to 22 equivalents, which is equal to about 7 per cent. of hydrochloric acid. The course of the numbers indicates that a part of the curve would show some deviation from a straight line, and that it would pass through a minimum-point at approximately an equal number of equivalents. Similar results were obtained with the chlorides of sodium, ammonium, strontium, and some other metals; but the minimum-point was not always reached when equal numbers of equivalents were used.

Investigations were made with sulphates and nitrates at a later time.[1] Sulphates were found to behave differently from chlorides; Engel formulates an approximate law as follows—addition of sulphuric acid decreases the solubility of the sulphates as if the acid removed from the solution and rendered inactive a quantity of water equal to that

[1] *Compt. rend.* **104**, p. 506 [1887]; *Ann. Chim. Phys.* (6) **17**, p. 338 [1889].

required to form the compound $H_2SO_4.12H_2O$; in other words, the sulphuric acid precipitates a quantity of sulphate proportional, but not equivalent, to the amount of acid added. This rule was proved for copper sulphate and cadmium sulphate; it did not hold for alkali sulphates, which are able to form acid sulphates.

The action of nitric acid was found to be, generally, of the same kind as that of hydrochloric acid; but the rule of equivalency was not followed in all cases, e.g. the solubility of potassium nitrate reached a minimum and then increased on addition of more nitric acid; a behaviour similar to this was noticed with stannous chloride and hydrochloric acid.[1]

That the foregoing phenomena are special cases of a general law which belongs to the domain of the chemical action of mass was pointed out by W. Nernst.[2]

21. **Solubilities of solids in mixtures of liquids.**—The addition to a solution of a liquid which is able to form a homogeneous whole with the solution causes precipitation of more or less of the substance in solution, if that substance is insoluble in the liquid which is added.

This fact is made use of in order to precipitate salts from their solutions, when evaporation is inadmissible; e.g. addition of alcohol to aqueous solutions of several salts causes precipitation of the salts. In these cases, the solid substance is less soluble in the mixture of two liquids than it is in the quantity of its own solvent contained in the mixture. Many measurements have been made by Wagner, Brandes, and others; most of them are concerned with mixtures of alcohol and water. Schiff[3] investigated the subject in a general way. He dissolved the salts in the following table in alcohol of 0, 10, 20, 30, 40, 50, 60, and 80 per cent. by weight, at 15°, and obtained the quantities of the various salts noted from 100 parts of the solutions :—

[1] *Compt. rend.* **105**, p. 1398 [1888].
[2] *Zeitschr. f. physikal. Chemie*, **4**, p. 372 [1889].
[3] *Annalen*, **118**, p. 362 [1861].

	0 p. ct.	10 p. ct.	20 p. ct.	30 p. ct.	40 p. ct.	50 p.ct.	60 p. ct.	80 p. ct.
KCl . .	24·6	19·8	14·7	10·7	7·7	5·0	2·8	0·45
NaCl . .	26·4	22·2	18·4	14·9	11·7	8·9	5·6	1·2
$BaCl_2.2H_2O$.	30·25	23·7	18·0	12·8	9·3	—	3·4	0·5
KNO_3 . .	20·5	13·2	8·5	5·6	4·3	2·8	1·7	0·4
$NaNO_3$ . .	45·9	39·5	32·8	26·2	20·5	—	10·2	2·7
K_2SO_4 . .	10·4	3·9	1·46	0·55	0·21	—	—	—
$Na_2SO_4.10H_2O$	25·6	14·35	5·6	—	1·3	—	—	—
$MgSO_4.7H_2O$.	50·8	39·3	21·3	—	1·62	—	—	—
$ZnSO_4.7H_2O$.	54·5	51·1	39·0	—	3·48	—	—	—
$MnSO_4$ . .	56·25	51·4	—	—	—	2·0	0·66	—
$FeSO_4.7H_2O$.	37·2	—	—	—	0·3	—	—	—
$CuSO_4.6H_2O$.	27·2	13·3	3·1	—	0·25	—	—	—

No relation could be traced between the decrease of solubility and the quantity of alcohol added; the quantity of salt which was precipitated from the aqueous solution by a specified quantity of alcohol varied much with the different salts; and the relation between the amounts of alcohol added and salt precipitated showed an approximate proportionality only for the salts KCl and $BaCl_2$, and $NaNO_3$ and NaCl. Nor did the results indicate that the alcohol withdrew a quantity of water from the solution corresponding with the formation of a definite hydrate, which then mixed with the saturated solution thus produced; for, if the quantity of water required to form a saturated solution was calculated from the amount of salt present, and the remaining water was supposed to be combined with alcohol, the proportion between these two quantities of water was found to vary.

The aqueous-alcoholic solutions of certain salts separate into two layers, one of which is a concentrated aqueous salt-solution containing a little alcohol, and the other is more concentrated alcohol containing a little of the salt; such salts are manganese sulphate and potassium carbonate. The laws of these phenomena are scarcely known as yet.

The problem examined by Schiff was attacked by A. Gerardin[1] in 1865. Many measurements were made, but the theory of the phenomena was not elucidated. Gerardin examined the solubilities of the salts NaCl, KCl,

[1] *Ann. Chim. Phys.* (4) 5, p. 129.

$BaCl_2$, $Pb(NO_3)_2$, $Ba(NO_3)_2$, NH_4Cl, K_2SO_4, KNO_3, KI, $SrCl_2$, and $Na\,C_2H_3O_2$, in eighteen different mixtures of water and alcohol containing from 94 to 5·2 per cent. alcohol, at different temperatures. One general result was that the character of the solubility-curve was the same for aqueous alcohol as for water. The solubility of potassium chloride, for instance, increased as temperature rose, and could be expressed by a simple equation. Thus, in water, $S = 29{\cdot}21 + {\cdot}29\,t$. The solubility of the same salt in aqueous alcohol was as follows :—

Per cent. Alcohol by Weight	Solubility
0	$28{\cdot}5 + {\cdot}29t$
5·2	$23{\cdot}2 + {\cdot}27t$
9·8	$19{\cdot}9 + {\cdot}255t$
15·4	$15{\cdot}7 + {\cdot}233t$
23	$11{\cdot}9 + {\cdot}205t$
35	$7{\cdot}1 + {\cdot}162t$
45	$4{\cdot}2 + {\cdot}125t$
65	$1{\cdot}89 + {\cdot}661t$

The same held good for barium chloride.

The solubility-curves of the other salts examined were nearly straight lines both for water and for mixtures of water and alcohol. The decrease in solubility was always greater than the decrease in the quantity of water in the alcohol ; addition of alcohol to the saturated aqueous solution, therefore, always produced precipitation ; the alcohol withdrew some of the water from the solution. Gerardin failed to find a general expression for this action of the alcohol. He noticed that the quantity of water thus withdrawn by the alcohol was small in the case of such easily soluble salts as KI, $NaC_2H_3O_2$, and $SrCl_2$; in these cases the decrease of solubility was nearly proportional to the quantity of alcohol in the solution. All the salts examined are insoluble in absolute alcohol.

There is one special, although isolated, observation which should be noticed. It is the existence of *corresponding temperatures*. If three temperatures are chosen at which

the three salts KNO_3, $Pb(NO_3)_2$, and $NaNO_3$ have equal solubilities in water, then the solubilities of these salts in dilute alcohol are also the same at the temperatures in question. The following numbers illustrate this point (decimals are unfortunately omitted by the author) :—

	Potassium Nitrate at 50°	Lead Nitrate at 58°	Sodium Nitrate at 18°
Water	86·3	86·1	86·1
„ + 5·2 p.ct. alcohol	72	72	72
„ +23 „ .	38	38	38
„ +65 „ .	6	6	6

A similar relation does not, however, hold good for other analogous salts—for instance, for chlorides.

CHAPTER V

OSMOSE

1. Generalities.—In preceding chapters were considered the different kinds of solutions, the conditions under which solutions are formed, and the relations which are established when equilibrium is attained between solutions and the substances from which they are formed.

But solutions may be regarded not only with reference to the conditions of their formation and their existence, but also with reference to the condition of the dissolved substances. In considering a mixture of two liquids, either may be regarded as the solvent and the other as the dissolved substance. To prevent any confusion of this kind, only those solutions will be considered in the following paragraphs wherein one of the substances is present in much larger quantity than the other; the substance present in large quantity will be called the solvent, and that present in relatively small quantity will be called the dissolved substance. In other words, we shall concern ourselves with *dilute* solutions.

The first fact to be noticed here is that when a solution of any substance is in contact with another solution of the same substance, of different concentration from the first, a condition of rest cannot generally be maintained. On the contrary, a movement of the dissolved substance begins, from the parts where it is present in larger quantity to the parts where it is present in smaller quantity, and this movement proceeds until the dissolved substance is distributed equally through the solution. If this move-

ment is hindered by the introduction of a partition, which is permeable by the solvent but not by the dissolved substance, the striving of the latter to permeate the whole solution makes itself apparent as a pressure against the partition. The phenomena noticeable in such a case are called *osmotic*.

2. **Earliest observations.**—In his book on Physics, which was held deservedly in high repute in the second half of the last century, the Abbé Nollet described an experiment to the effect that if a glass vessel is filled with spirits of wine, and the opening is tightly covered with a bladder, and the whole is then immersed in water, the contents of the vessel increase so that the bladder is expanded and is sometimes burst. This experiment was forgotten for many years; it was brought to light again by F. Parrot [1] in 1815. Parrot ascribed the phenomena to a special force which he called 'affinity of the first degree;' he recognised this to be of a perfectly general character, *inasmuch as all miscible liquids show a tendency to 'wander' one into the other when they are brought into contact, and this process continues until the liquids are perfectly equally distributed.* Parrot also established the fact that the presence of a membrane, as used by Nollet, is not a necessary condition of the action, since the spontaneous admixture of the liquids proceeds more readily when they are brought into free contact one with the other. Parrot was fully aware of the important bearing of the phenomena on processes which occur in living organisms.

The second discovery of these facts did not suffice to make them the common property of science. They were discovered a third time by N. W. Fischer [2] in Germany, and a fourth time by Dutrochet [3] in France; it was only after this that the investigation of these facts was earnestly taken up. The greatest interest centred round the changes of level which occurred when two different liquids, such as water and a salt solution, separated by an animal

[1] *Gilb. Ann.* **51**, p. 318. [2] *Ibid.* **72**, p. 300 [1822].
[3] *Ann. Chim. Phys.* (2) **35**, p. 393 [1827].

membrane, were kept in contact. The existence of the membrane was regarded as essential; the older investigators carried out many experiments with membranes, but without arriving at results of a general character.[1]

3. **Membranes formed by precipitation.**—The animal bladders which were used by the older investigators were insufficient aids for studying the fundamental phenomena. These bladders, it is true, allowed only the very slow passage through them of the dissolved substance; but the passage was only hindered, it was not stopped, and even the degree of hindrance depended on the condition of the membrane. The possibility of obtaining membranes which should be quite impermeable by the dissolved substance, was suggested by M. Traube,[2] as a result of his experimental examination of the causes which lead to the formation of cells. When solutions of certain substances which form precipitates with one another are carefully brought into contact, a hard pellicle is formed at the surface of separation of the liquids; this pellicle is permeable by water, but not by certain other substances, among which are the two reagents by whose mutual action the pellicle has been formed.[3]

4. **Investigations of W. Pfeffer.**—Traube showed that certain substances are able to pass through membranes formed by precipitation, and that certain other substances do not pass through these membranes, and that, generally speaking, equilibrium does not occur between two solutions of membrane-forming substances, inasmuch as the cells, produced by the contact of the solutions, show a tendency either to increase or decrease in size, and therefore a

[1] Magnus, *Pogg*, **10**, p. 160 [1827]; Jerichau, *Pogg.* **34**, p. 613 [1835]; Brücke, *Pogg.* **58**, p. 77 [1843]; Liebig, *Über einige Ursachen der Säftebewegung in tierischen Organismus*, Braunschweig, 1848; Vierodt, *Pogg.* **73**, p. 519 [1848]; Jolly, *Pogg.* **78**, p. 261 [1849]; Ludwig, *Pogg.* **78**, p. 307 [1849].

[2] *Archiv. f. Anat. und Physiol.* 1867, p. 87.

[3] A long quotation from Traube is given here in the original.—*Translator.*

pressure is produced either from within or from without. Traube did not succeed in measuring the pressures thus exerted, because of the small resistance of the membranes he used.

Pfeffer [1] was the first to solve this part of the problem; he used membranes produced by precipitation within a partition capable of considerable resistance, but in other respects porous. The very careful manipulation required is described by Pfeffer as follows:—

'The apparatus is represented in fig. 16, about one-half the natural size, with the manometer, *m*, attached; the clay-cell, *z*, and the glass tubes, *v* and *t*, are drawn in section. The clay-cells used by me were generally about 46 mm. high, and 16 mm. diameter, and the walls were about $1\frac{1}{4}$ to 2 mm. thick. The narrower glass-tube, *v*, was fastened into the cell by means of sealing-wax, and the tube, *t*, was sealed into the other end of *v* in the same way. The glass-ring, *r*, was required only for experiments at high temperatures. . . . With certain precautions, it is not difficult to make the sealing-wax joints capable of withstanding considerable pressure; the greatest care must be used in making the joint between the clay-cell and the tube *v*. For experiments at, and below, ordinary temperatures, the cylindrical space between *v* and the cell was filled with two sorts of sealing-wax; the greater part of this space was filled with comparatively infusible packing sealing-wax, and this was fitted closely to an under-ring of sealing-wax, placed towards the interior of the cell, and softened before use by means of turpentine or liquid pitch. Only this inner ring, the consistency of which prevented the formation of small channels or rifts, was in contact with the membrane produced by precipitation within the cell. The more solid sealing-wax served to prevent the pushing out of the tube *v* by the pressure produced in an experiment. To make this double-joint, the glass tube *v* is placed in the clay-cell along with the less fusible sealing-wax, the wax which is thus extruded is removed by a properly-formed instrument, the more liquid sealing-wax is added, and while this is molten, the tube is pushed farther into the cell. The results of different experiments may be

[1] *Osmotische Untersuchungen*, Leipzig, 1877.

discordant unless very great care is taken to make the connexion between the sealing-wax and the cell perfectly sound, and to ensure that the surface of the ring of softer wax in the interior of the cell is smooth and even. I have made use of the short tube *v*, because this allows the interior of the cell to be seen; and the firm fixing in of the tube *t* can also be accomplished with ease and certainty. Before the adjustments were made, all the clay-cells were treated with dilute potash, and then with dilute hydrochloric acid (about 3 per cent.); they were then well washed with water, and thoroughly dried. Substances which were soluble in the liquids used, and which might exert a hurtful action in the experiments, were thus removed, notably earths and iron salts.

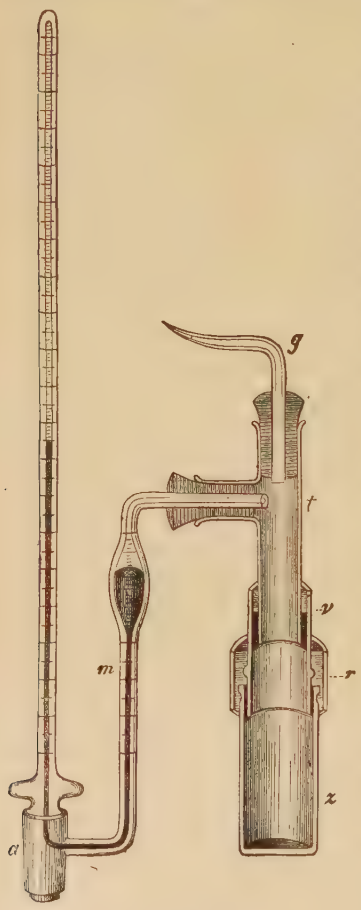


Fig. 16

'As I experimented chiefly with membranes of copper ferrocyanide, deposited on the inner surface of the cells, I shall describe the preparation of these membranes in detail.

'The cells were thoroughly saturated with water, by repeated evacuation under the air-pump; they were then filled with a three per cent. solution of copper sulphate, and placed for several hours in a quantity of the same solution. The interiors of the cells were then rapidly washed out several times with water, and well dried as quickly as possible by means of slips of filter paper; the exteriors were now partially dried; the cells were allowed to stand in the air until they felt just moist, when a three per cent. solution of potassium ferrocyanide was poured into

them, and they were at once placed again in the solution of copper sulphate. After twenty-four to forty-eight hours the cells were completely filled with the potassium ferrocyanide solution, and they were then closed in the manner indicated in fig. 16. As the osmotic effect of potassium ferrocyanide solution is somewhat greater than that of copper sulphate solution, a pressure from within the cell in the outward direction was gradually produced. After another period of twenty-four to forty-eight hours the apparatus was opened, and, in most cases, a solution of 3 per cent. potassium ferrocyanide and $1\frac{1}{2}$ per cent. potassium nitrate (by weight) was poured in; this solution produced an osmotic pressure of more than three atmospheres. The rise of pressure should at first be slow, and this smaller pressure should be maintained for a certain time; experience has shown that these are indications that the apparatus is fit for use. If the foregoing directions are carried out with care, the preparation of workable cells can be accomplished with certainty. In my later work, hardly one cell out of twenty has failed; but at first I had many difficulties to contend with, and I was scarcely able to make any properly deposited membranes before I had recourse to the expedient of partially drying the cells.'

The most noticeable phenomenon which Pfeffer observed by means of his apparatus was the production of high pressures within the clay-cells, when these cells were filled with certain solutions and were then placed in pure water. It has already been remarked that a solution containing $1\frac{1}{2}$ per cent. of nitre produced an 'osmotic pressure' of more than three atmospheres.

Pfeffer's observations also showed that this pressure is intimately connected with the nature of the dissolved substance. One per cent. solutions of the following substances produced the pressures noted; the pressures are measured in centims. of mercury:—

Cane-sugar	47·1 centim.	Potassium sulphate	193 centim.
Dextrin	16·6 „	Gum	7·2 „
Nitre	178 „		

Further, the pressure was found to be dependent on, and proportional to, the concentration of the solutions. Most

of the experiments were carried out with cane-sugar; the following table shows the results:—

Per cent. Sugar in Solution	Pressure, in centim. of Mercury	Pressure, per cent. of Sugar
1	53·8	53·8
1	53·2	53·2
2	101·6	50·8
2·74	151·3	55·4
4	208·2	52·1
6	307·5	51·3
1	53·5	53·5

The numbers in the last column range irregularly round a mean value, and show that pressure and concentration are proportional. Similar results were obtained with gum, and with nitre:—

	Per cent.	Pressure	Pressure, per cent.
Gum	1	7·2	7·2
	18	119·7	6·7
	18	120·4	6·7
Nitre	·8	130·4	163
	1·43	218·5	153
	3·3	436·8	133
	·86	147·5	171

In the case of nitre, the ratio of pressure to percentage decreases notably as concentration increases. The reason for this is that it was very difficult to obtain a membrane which should be perfectly firm at the great pressure (nearly 5·8 atmospheres) produced at the beginning of the experiment; and also, and more especially, as Pfeffer showed, the membrane used was not quite impervious to nitre, so that this salt could not produce its complete effect in increasing the pressure.

The pressure, at a specified concentration, was also found to be dependent on the temperature; as the temperature rose, the pressure increased regularly. A series of experiments with one per cent. cane-sugar gave the following results:—

Temp.	Pressure	Temp.	Pressure
6·8°	50·5	14·2°	53·1
13·2	52·1	22	54·8
13·8	52·2		

Lastly, Pfeffer conducted some experiments with other membranes. A solution of cane-sugar which gave a pressure of about 52 centims. with a copper ferrocyanide membrane, produced a pressure of 37 to 40 centims. with a membrane of Prussian blue, and a pressure of 36 centims. with a membrane of calcium phosphate; the temperature being 13° to 15°.

5. **Theoretical importance of the investigations of Pfeffer.**—The significance of the phenomena described in the preceding paragraph in their bearing on the nature of solutions remained for long unnoticed. The discoverer required the facts only for the elucidation of the physiological questions with which he was concerned; he contented himself with making a few remarks on the causes of the phenomena he had observed. It was not until 1885 that van 't Hoff[1] began to develop a theory of solutions on the basis of these phenomena; this theory has already proved itself, and continues to prove itself, to be eminently fruitful.

The investigations of Pfeffer experimentally establish the fact that when a solution is separated from pure water by a partition which allows water to pass through it with comparative ease, but is impervious to the substance in solution, a pressure is noticeable which is dependent on the nature of the dissolved substance and the temperature, and increases proportionally to the concentration. There is no doubt that the cause of this pressure is to be sought for in the dissolved substance, for the water cannot produce any enduring pressure, inasmuch as it passes through the separating membrane without difficulty. Moreover, the

[1] *Archiv. Néerland.* **20**; *K. Svensk Ak. Hand.* **21**. A general account is given in *Zeitschr. f. physikal. Chemie*, **1**, p. 481 [1887]; a translation of this paper appeared in *Phil. Mag.* August 1888.

circumstance that the pressure increases in proportion to the concentration of the dissolved substance is evidence that pressure and concentration are causally connected, that the pressure is originated by the substance in solution. The separating wall is not the cause of the pressure, but it is the condition which makes the pressure appreciable and measurable. For in the investigation already described the outward pressure of the liquids is the same, at the outset, both within and without the cell. But this condition cannot persist. The cell behaves as if there were a partial vacuum for water in its interior; water flows in, and, if no opposing pressure is allowed to develop, produces a continuous movement which ceases only when the contents of the cell have become the same as those of the space surrounding the cell, i.e. have become pure water. A condition of equilibrium is possible only when the pressure which prevails within differs sufficiently from that which prevails without. The first part of the phenomenon always occurs when a solution and pure water are brought into contact without a separating wall; a movement of the dissolved substance into the water occurs, and this movement does not cease until the substance is equally distributed. Now in order to accomplish such a movement, there must be a corresponding cause, or force, residing in the particles of the dissolved substance. This becomes noticeable when the motion of the particles in the direction of the force is hindered by the membrane in the cell, but it is present when the membrane is not there, as otherwise there would be no cause for the movement of the particles.

We are able, then, to distinguish between two classes of occurrences : the pressure-phenomena, or the osmotic phenomena, which are caused by the forces at work in the particles of the dissolved substance; and the occurrence of movements, or the phenomena of diffusion, which have the same cause. The latter class will be considered in the next chapter.

6. **Connexion between the pressure and the nature of the membrane.**—It would seem to follow from some of Pfeffer's experiments that the nature of the membrane exerts a considerable influence on the magnitude of the osmotic pressure which a solution exhibits against pure water. For instance, a one per cent. sugar solution showed a pressure equal to 52 centims. of mercury with a membrane of copper ferrocyanide, whereas with a membrane of Prussian blue the pressure was 37 to 40 centims., and with a membrane of calcium phosphate the pressure was 36 centims. But nevertheless it may be stated with certainty that *the amount of pressure is independent of the nature of the membrane*, provided that the membrane is not permeable by the dissolved substance. To understand this, let it be supposed that two separating partitions, A and B, formed of different membranes, are placed in a cylinder (fig. 17). Let the space between the membranes contain a solution and let there be pure water in the space at the ends of the cylinder. Let the membrane A show a higher pressure, P, and the membrane B show a smaller pressure, p. At the outset, water will pass through both membranes into the inner space until the pressure p is attained, when the passage of water through B will cease, but the passage through A will continue. As soon as the pressure in the inner space has been thus increased above p, water will be pressed out through B. The pressure can never reach the value P; water must enter continuously through A, while a finite difference of pressures is maintained. If this were realised we should have a machine capable of performing infinite work, which is impossible. A similar demonstration holds good if $p > P$; it is, therefore, necessary that $p = P$; in other words, it follows necessarily that *osmotic*

FIG. 17

pressure is independent of the nature of the membrane. Pfeffer's results, which were opposed to this conclusion, are to be accounted for either by the membrane not being thoroughly firm, or by the passage through it of a small quantity of sugar. Pfeffer puts forward the experiments in question only as provisional, and does not place any great weight on the actual numbers.

The conclusion that osmotic pressure is independent of the nature of the membrane is important, because it shows that this pressure is a specific property of the substance in solution, dependent upon the nature of this substance, and that in this respect it resembles gaseous pressure, which likewise is independent of the nature of the containing vessel.

7. **Other investigations.**—Since the appearance of Pfeffer's work, the direct measurements of osmotic pressures have not been made the subject of systematic investigation.[1] Nevertheless, our knowledge of the subject has been extended by some indirect methods of investigation; these methods are described in the sequel.

The work of H. de Vries,[2] carried out for physiological purposes, must be mentioned first. Pringsheim, in 1854, made the observation that the protoplasmic contents of an organic cell contract when the cell is brought into concentrated salt-solutions. As the outer cell-wall retains its form, the phenomena seem to show that the protoplasmic contents draw together into the form of a spherical mass which remains connected with the cell-wall by a few filaments, while the space between the granular, and occasionally coloured, protoplasm and the cell-wall is filled with the transparent solution which has entered the cell. See fig. 18, c.

The cause of this process is found in the fact that the protoplasm is covered with a little membrane, which

[1] Some communications of a preliminary character have been made public by Ladenburg (*Berichte*, **22**, p. 1225 [1889]), but no details have yet been given.

[2] *Pringsheim's Jahrbücher*, **14**, p. 427 [1884].

possesses, most markedly, the property of membranes produced by precipitation of being pervious to water, but impervious to most dissolved substances. If, therefore, the exterior solution has a greater osmotic pressure than the protoplasmic contents of the cell, the cell-contents will be compressed, with loss of water, and will assume the form already described. Such compression will take place to a less extent if a less concentrated solution is used; in this case the protoplasm will be loosened at some of the

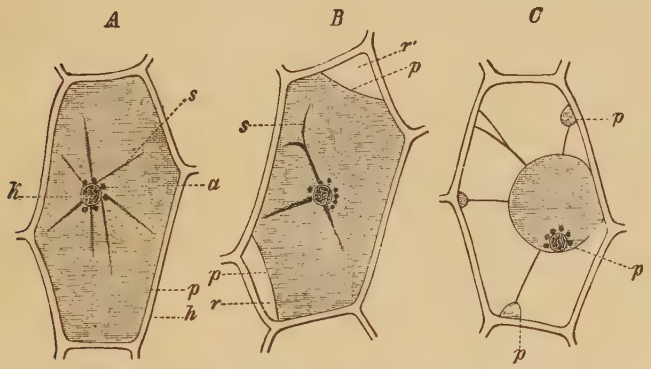


Fig. 18.—Cells from the epidermis of the mid-rib of a leaf of *Tradescantia discolor*, magnified 300 times.

A=normal cell; B=plasmolysis in solution of ·22 mols. cane-sugar; C=very marked plasmolysis in solution of 1 mol. nitre; *k*=cell-nucleus; *s*=protoplasmic filaments; *h*=cell-wall. The cell-sap *p* (darkened in the figure) is coloured violet.

corners of the cell (fig. 18, B). If the osmotic pressure of the exterior liquid is equal to, or is less than, that of the cell-contents, the protoplasm will maintain its form and will cling closely to the cell-wall (fig. 18, A).

By examining the action of the solution of any substance on a cell of the kind described, the solution being made gradually more dilute, it is possible to find a concentration whereat the solution has the same osmotic pressure as that of the contents of the cell. If the concentrations of a normal substance and another substance under examination are adjusted, by means of cells of the same kind, so that both solutions are in osmotic equilibrium with the contents of the cells, then the two solutions possess

equal osmotic pressures, or, to use a term introduced by de Vries, the solutions are *isotonic*.

It is not easy to find cells suitable for an investigation of this kind; de Vries found only three plants from which suitable cells could be obtained. The contents of the cells must be coloured, in order that the loosening of the protoplasm may be observed with precision; the loosening must occur at the sides of the cells, else it is not easily seen; and, lastly, and this is a condition very difficult to realise, all the cells of one preparation must show equal osmotic pressures in each direction, because quite a number of cells may be used for a series of experiments, and it is necessary to assume equal pressures for all. The most suitable cells are the following:—the cells of the epidermis on the under side of the mid-rib of the leaves of *Tradescantia discolor*, the exterior cells of the spathe of *Curcuma rubricaulis*, and the cells from the highest scales of the leaf-stalk of *Begonia manicata*. *Begonia* is the least serviceable, but it allows the use of dilute organic acids, which cannot be employed with the others.

The experimental method of de Vries takes for granted a point which ought to be stated explicitly; it is assumed that two solutions which are isotonic with a third (the cell-sap) must also be isotonic with one another. The statement is proved experimentally by the fact that the same proportion is found for the concentrations of isotonic solutions whatever be the kind of cells employed or the nature of the contents of the cells. But the statement may be proved, in a general way, by using a method of proof similar to that employed in the last paragraph (p. 103). If two solutions could be obtained which were isotonic with a third solution, but were not isotonic with one another, it would be easy, with the help of these solutions, to construct a machine from which an endless quantity of work should be obtained; but this is impossible.

The results of the work of de Vries are as follows. The forces of osmotic pressure which are exhibited by solutions are

proportional to the concentration of the dissolved substance. These forces are connected with the chemical nature of the substance in solution, so that equimolecular solutions of similar substances, i.e. solutions which contain quantities of the substances proportional to their molecular weights dissolved in the same quantity of water, exhibit equal osmotic pressures, or are isotonic. The memoir of de Vries contains the following numbers:—

	(1)	(2)		(1)	(2)
Cane-sugar	1·88	1·84	Potassium oxalate		3·93
Inverted sugar	1·88	1·84	„ sulphate	3·9	3·92
Malic acid	1·98		Di-potassium phosphate		3·96
Tartaric „	2·02		Potassium tartrate		3·99
Citric „	2·02		„ malate		4·11
Potassium nitrate	3·0	3·0	Di-potassium citrate	4·08	
Sodium „	3·0		Potassium „	5·01	4·74
Potassium chloride	3·0	2·84	Magnesium malate	1·88	1·63
Sodium „		3·05	„ sulphate	1·96	1·78
Ammonium „	3·0		„ citrate	3·88	3·53
Potassium acetate	3·0		„ chloride	4·33	
Mono-potassium citrate	3·05		Calcium chloride	4·33	

The osmotic pressure of potassium nitrate, taken as 3, is adopted as the unit of reference for the other values. The meaning of the numbers is that the osmotic pressure of the solution of a specified substance is related to that of potassium nitrate solution in the ratio of the number placed opposite the specified substance to 3; e.g. the osmotic pressures of equimolecular solutions of cane-sugar and potassium nitrate are in the ratio 1·88 : 3. The molecular contents of a solution of cane-sugar which is isotonic with a solution of nitre must, therefore, be $\frac{3\cdot0}{1\cdot88} = 1\cdot6$ times greater than that of the nitre solution. From the results he obtained, de Vries concluded that the 'isotonic coefficients' of substances are whole numbers, and stand to one another in the ratio of such whole numbers as 2 : 3 : 4 : 5, provided the value for nitre be taken as 3. This generalisation may be passed over with the remark that the values obtained by de Vries

have shown themselves to be more exact than the observed deviations from his rule would lead one to suppose. But it appears that the osmotic pressures of chemically similar substances are nearly equal. The substances examined may be divided into organic compounds with coefficients approximately equal to 2, salts R′A′ (composed of a monad metal R′ and a monad acidic radicle A′) with the value 3, salts R'_2A'' with the value 4, salts R'_3A''' with a value about equal to 5, salts R″A″ with approximately the value 2, and finally salts $R''A_2'$ with the coefficient 4·3.

Besides the method of investigation already described, called by de Vries the 'plasmolytic' method, de Vries used two other processes, the 'plasmolytic transport method,' and the method of 'tissue-stress' (*Gewebespannung*). As only the first method need be noticed for our purpose, it will suffice to remark here that the other methods led to the same numerical values as the plasmolytic method. The numbers in the second column of the preceding table were obtained by the method of tissue-stress.

Some further determinations of isotonic coefficients have been made more recently by de Vries.[1] These results are given in the opposite table;[2] the last column contains results obtained by another method by Donders and Hamburger (see par. 9).

8. **Optical methods.**—A process, based on the use of Topler's apparatus for detecting small changes in the refractive powers of liquids,[3] has been applied by G. Tammann[4] to determine the equality of the osmotic pressures of two different liquids, and thus to adjust one liquid so that it shall be isotonic, or 'isomotic,' with another. When a membrane has been formed in a cell, by Traube's method, by means of potassium ferrocyanide and copper sulphate solutions, either the inner or the outer

[1] *Zeitschr. f. physikal. Chemie*, **2**, p. 415 [1888]; **3**, p. 103[1889].
[2] *Botan. Zeitung*, 1888, Nos. 15 & 16.
[3] *Pogg.* **131**, p. 33 [1867].
[4] *Wied. Ann.* **34**, p. 299 [1888].

ISOTONIC COEFFICIENTS.

Substance	Formula	Isotonic Coefficients by			
		The plasmolytic method	The transport method	The tissue-stress method	The method of blood corpuscles
Group I.					
Glycerin	$C_3H_8O_3$	1·78	—	—	—
Invert Sugar	$C_6H_{12}O_6$	1·88	—	1·84	—
Cane-Sugar	$C_{12}H_{22}O_{11}$	1·81	1·95	1·84	1·72
Group II.					
Malic acid	$C_4H_6O_5$	1·98	—	—	—
Tartaric „	$C_4H_6O_6$	2·02	—	—	—
Citric „	$C_6H_8O_7$	2·02	—	—	—
Group III.					
Magnesium malate	$MgC_4H_5O_5$	1·88	—	1·63	—
„ sulphate	$MgSO_4$	1·96	—	1·78	2·44
Group IV.					
Potassium nitrate	KNO_3	3·0	—	—	3·0
Sodium „	$NaNO_3$	3·0	—	—	—
Potassium chloride	KCl	—	3·0	2·84	—
Sodium „	NaCl	3·0	—	3·05	3·0
Ammonium „	NH_4Cl	—	—	—	—
Potassium iodide	KI	—	—	—	3·04
Sodium „	NaI	—	—	—	2·90
Potassium bromide	KBr	—	—	—	3·05
Sodium „	NaBr	—	—	—	3·03
Potassium acetate	$KC_2H_3O_2$	3·0	—	—	2·85
Mono-potassium citrate	$KH_2C_6H_5O_7$	3·05	—	—	—
Group V.					
Potassium oxalate	$K_2C_2O_4$	—	—	3·93	4·07
„ sulphate	K_2SO_4	—	3·9	3·92	4·7
Di-potassium phosphate	K_2HPO_4	—	—	3·96	—
Potassium tartrate	$K_2C_4H_4O_6$	—	—	3·99	—
„ malate	$K_2C_4H_4O_5$	—	—	4·11	—
Di-potassium citrate	$K_2HC_6H_5O_7$	4·08	—	—	—
Group VI.					
Calcium chloride	$CaCl_2$	4·33	—	—	4·05
Magnesium „	$MgCl_2$	4·33	—	—	3·84
Barium „	$BaCl_2$	—	—	—	4·03
Magnesium citrate	$Mg_3(C_6H_5O_7)_2$	3·88	—	3·53	—
Group VII.					
Potassium citrate	$K_3C_6H_5O_7$	5·01	—	4·74	—

liquid generally shows a greater pressure than the other. If the pressure of the inner liquid is the greater, water passes from the outer solution into the cell, the liquid around the cell becomes more concentrated, and, on account of its greater specific gravity, this more concentrated liquid flows downwards. On the other hand, if the pressure of the outer liquid is the greater, water passes outwards, the liquid surrounding the cell becomes more dilute and flows upwards. These changes may be observed by the use of Topler's apparatus by which very minute differences between the refractive powers of two liquids may be detected. It is thus possible to adjust one liquid to another so that water shall neither flow inwards nor outwards through the cell-walls, and both liquids shall therefore have the same osmotic pressure.

The different concentrations of the membrane-forming substances may be compared by this method. Tammann found the only suitable membranes to be those of copper and zinc ferrocyanide; hence his investigations were confined to determining the isotonic solutions of copper and zinc salts in comparison with ferrocyanides.

The method might be extended, however, by adding to the membrane-forming solutions different quantities of a third substance (which must be without chemical action on the membrane-forming substance) and then finding the concentration of the second membrane-former which was isotonic with this mixed solution. That part of the osmotic pressure which was due to the substance added could then be calculated, on the supposition, the accuracy of which it would be possible to establish by the experiments themselves, that the osmotic pressure of the mixed substances was the sum of the pressures of each.

The following numbers, selected from Tammann's results, represent molecular concentrations, i.e. the number of gram-molecular weights dissolved in 1,000 grams of water; the ratio of the numbers is given in the column v :—

$CuSO_4$	$K_4Fe(CN)_6$	v	$Cu(C_2H_3O_2)_2$	$K_4Fe(CN)_6$	v
0·842	0·313	2·7	0·338	0·203	1·67
0·675	0·240	2·8	0·240	0·147	1·63
0·339	0·117	2·9	0·167	0·108	1·55
0·204	0·079	2·6	0·111	0·074	1·50
0·170	0·066	2·6	0·055	0·039	1·41
0·094	0·036	2·6			

$CuCl_2$	$K_4Fe(CN)_6$	v	$Cu(NO_3)_2$	$K_4Fe(CN)_6$	v
0·476	0·512	0·93	0·554	0·586	0·94
0·379	0·397	0·95	0·439	0·439	1·00
0·313	0·319	0·98	0·364	0·351	1·04
0·236	0·230	1·02	0·272	0·251	1·08
0·157	0·146	1·08	0·185	0·158	1·18
0·094	0·086	1·09	0·108	0·088	1·22
0·043	0·033	1·30	0·049	0·036	1·36

$ZnSO_4$	$K_4Fe(CN)_6$	v	$ZnCl_2$	$K_4Fe(CN)_6$	v
1·280	0·549	2·3	0·440	0·473	0·93
1·023	0·410	2·5	0·329	0·352	0·93
0·851	0·329	2·6	0·219	0·216	1·01
0·638	0·234	2·7	0·131	0·127	1·03
0·425	0·155	2·4	0·060	0·070	0·86
0·266	0·126	2·1			
0·101	0·061	1·7			

The irregular deviations show that the numbers are affected by errors of considerable magnitude. Nevertheless, it is evident that the ratio of the isotonic concentrations does not change much with increasing dilution; the ratio generally increases somewhat. Similar salts, such as $CuSO_4$ and $ZnSO_4$, $CuCl_2$ $Cu(NO_3)_2$ and $CuCl_2$, show very similar proportional numbers when compared with the isotonic concentrations of ferrocyanides.

From the results with other substances, most of which were organic compounds, it may be concluded that equimolecular solutions of these show osmotic pressures which are equal within the limits of experimental error. The substances examined thus were cane-sugar, salicin, ethyl

alcohol, chloral hydrate, ether, ethyl acetate, isobutyl alcohol, urea, and propyl alcohol.

Tammann emphasises the point that solutions which have equal osmotic pressures also exhibit equal vapour-pressures. This statement had been deduced by van 't Hoff, by theoretical reasoning, shortly before the publication of Tammann's work. The questions connected with this assertion will be considered later in their proper connexion.

9. **Influence of temperature.**—Donders and Hamburger [1] determined isotonic coefficients by a method very similar to that used by de Vries, but they employed blood-cells in place of cells of plants; their results are given in the last column of the table on p. 109.

These results showed a noteworthy advance, inasmuch as they were obtained for two fairly different temperatures viz. 0°, and 34° (the temperature of blood). The numbers showed that solutions which were isotonic at the lower temperature were also isotonic at the higher temperature. As one result of the direct experiments of Pfeffer is that osmotic pressure increases with increasing temperature, it follows that *the increase of osmotic pressure which accompanies an increase of temperature is independent of the nature of the dissolved substance.*

It should be noted at once that there are exceptions to this statement, but the number of these is not great; just as the expansion-coefficient of gases has not invariably the same value. The statement holds good in by far the greater number of cases.

The common temperature-function of osmotic pressure might be determined by the method of Pfeffer, if the experiments were conducted in a sufficiently accurate manner. But the determination presents very great experimental difficulties at present. Meanwhile the function may be deduced thermodynamically, by the method

[1] *Onderz. Physiol. Lab. Utrecht* (3), **9**, p. 26; cf. Hamburger, *Zeitschr. f. physikal. Chemie*, **6**, p. 319 [1890].

shown to be applicable by van 't Hoff.[1] The proof rests on the statement that in a reversible cyclical change, which proceeds between the temperatures T and $T - dT$, the portion of the total heat which is convertible into work is $Q\frac{dT}{T}$, where Q = total quantity of heat.

Let the solution, with volume v and osmotic pressure p, be placed in a cylinder, fitted with a movable piston, and closed at one end by a membrane which allows the passage of water, but prevents the passage of the substance in solution. The piston is held in position by a pressure equal and opposite to the osmotic pressure. If this opposing pressure is decreased by an infinitely small amount, water penetrates the membrane, the piston is raised and performs the work $p\,dv$, while the volume-increase is represented by dv. During this process the temperature remains constant; to do this a quantity of heat, Q, equal to the work done, $p\,dv$, must be added Now let the piston move further, but let no more heat be added; the temperature sinks to $T - dT$, and the pressure to $p - \frac{dp}{dT}\,dT$. At this lower pressure, the piston is pressed down into the cylinder until a change of volume $= dv$ is attained, and the heat produced is removed so that the temperature remains at $T - dT$. Finally, the removal of heat is stopped, and the compression is continued until the temperature rises to T, and the original volume v is attained. The cyclical process is now stopped.[2]

The heat added was $Q = p\,dv$; the fraction of this which is convertible into work is the difference between the two quantities of work $p\,dv$ and $\left(p - \frac{dp}{dT}\,dT\right)dv$, and is therefore $= \left(\frac{dp}{dT}\right)dT\,dv$.

[1] *Zeitschr. f. physikal. Chemie*, 1, p. 485 [1887].

[2] The subject of the second law of thermodynamics may be studied in Clausius' *Mechanical Theory of Heat.*

Then, from the general statement enunciated above, we have

$$\frac{d\mathrm{T}}{\mathrm{T}} = \frac{\frac{dp}{d\mathrm{T}} . d\mathrm{T}\, dv}{p\, dv}$$

$$\text{or } \frac{p}{\mathrm{T}} = \frac{dp}{d\mathrm{T}}$$

and by integration

$$p = c\mathrm{T}$$

where c is the integration-constant.

Hence *osmotic pressure is proportional to the absolute temperature.*

The results obtained by Pfeffer agree, on the whole, with this conclusion, within the limits of experimental error. The following numbers show this :—

	$t°$	Observed	$t'°$	Observed	Calculated
Cane-sugar . . .	32°	54·4	14·2°	51·0	51·2
,, . . .	36	56·7	15·5	52·1	52·9
Sodium tartrate . .	36·6	156·4	13·3	143·2	144·3
,, . . .	37·3	98·3	13·3	90·8	90·7

The numbers under the heading *calculated* show the pressures calculated for the lower temperatures, t', from those observed at the higher temperatures, t, on the assumption that pressure is proportional to absolute temperature. The agreement between the pressures observed at the lower temperatures and those calculated for these temperatures is very close ; but it must not be concealed that other results obtained by Pfeffer show much less agreement than those quoted above. The experimental errors are so large that no great weight can be put on either the one or the other set of results.

10. **Analogy between the state of solution and the gaseous state.**—Putting together the laws which are known to express the phenomena of osmotic pressure, we have the following relations :—

1. The pressure is proportional to the concentration, or it is inversely proportional to the volume in which a definite quantity of the dissolved substance is contained.

2. The pressure increases, for constant volume, proportionally to the absolute temperature.

3. Quantities of dissolved substances which are in the ratio of the molecular weights of these substances exert equal pressures at equal temperatures.[1]

The analogy between these three laws and the gaseous laws is very evident. The first law corresponds with the law of Boyle, the second with the law of Charles (or Gay-Lussac), and the third with the law of Avogadro. To van 't Hoff[2] is due the merit of being the first to insist on this analogy, and to draw the weighty conclusions which this resemblance makes possible.

At the outset it is necessary to find an answer to the question which asks what real ground there is for the analogy. The answer is to be found in the same cause as lies at the root of the simple gaseous laws which are independent of the composition of the different gases. As in gases, so in dilute solutions, the molecules of the substances are so far apart that only those properties come into importance which depend on the number of the molecules, while those properties which depend on their individual nature in many cases disappear. Following a proposal made by W. Wundts, I shall apply the term *colligative*[3] to properties of this kind; the volume- and pressure-relations of gases are the classical example of such properties. The appearance of properties of this kind is a peculiarity of matter when the parts are widely separated from one another so that the mutual actions of these parts are reduced to a minimum.

The analogy between gases and solutions may be followed further, as was shown by van 't Hoff. The numerical

[1] This statement holds good only for indifferent substances. The exceptions will be discussed later.

[2] *Zeitschr. f. physikal. Chemie*, 1, p. 481 [1887]. [3] See note on p. 30.

value of the pressure exerted by a quantity of a gas, the weight of which in grams is equal to the molecular weight of the gas, was already found[1] to be expressed by the formula $pv = RT$, where $R = 84{,}700 =$ a constant independent of the nature of the gas.

Pfeffer's most numerous and accurate measurements were made with cane-sugar; a solution containing 1 per cent. of this compound was found to exert an osmotic pressure at 0° equal to 49·3 centims. of mercury. The pressure in grams per square centim. is equal to 49·3 × 1033. The volume in which a gram-molecular weight of cane-sugar is contained in a 1 per cent. solution is 34,200 c.c., inasmuch as the molecular weight of $C_{12}H_{22}O_{11}$ is 342. The temperature is 273°, in absolute measure. Substituting these values, R is found to be 84,200; this number agrees with the constant for gases within the limits of experimental error. Inasmuch as the osmotic pressures of equimolecular solutions are equal, the same constant must be found for every other substance. The following statement, therefore, follows:— *Dissolved substances exert the same pressure, in the form of osmotic pressure, as they would exert were they gasified, at the same temperature, without change of volume.*

We are, therefore, warranted in carrying over to solutions, without change of constant, all that we know to hold good for the properties of gases, so far as these are dependent on pressure, volume, and temperature, provided only that osmotic pressure be substituted for the ordinary pressure of gases.

The assertion that pressures of very considerable magnitude must exist in moderately concentrated solutions, appears at first sight somewhat astonishing. It is easily calculated, from the equation given above, that a solution containing 17 per cent. of ammonia must exert against pure water, at 0°, an osmotic pressure not less than 224 atmospheres. It has been asked, in all seriousness, why such a solution does not break the vessel in which it is placed.

[1] This formula is discussed in an early part of the *Lehrbuch.—Translator.*

Such a solution would break the vessel containing it if the walls of that vessel were permeable by water, but not by ammonia, and this vessel were placed in pure water. Phenomena of this kind are observed in the destruction of the walls of cells with somewhat concentrated protoplasmic contents, when such cells are placed in pure water. The pressure cannot, however, make itself felt towards the exterior of the solution, because it is opposed on the surface by the normal interior pressure, which prevails in every liquid, and which is measured in thousands of atmospheres. The osmotic pressure can show itself only by diminishing this interior pressure and so slightly increasing the volume of the liquid; it can never come into play towards the exterior of the liquid, because it is always quite overpowered by the interior pressure.

It follows, from this way of regarding the subject, that when a liquid is diluted, the total volume must generally become somewhat smaller. For, suppose the liquid is diluted to twice the original volume, then the interior pressure is opposed by an osmotic pressure equal to one-half the pressure before dilution, and therefore the total volume must decrease to an amount corresponding with this decrease of osmotic pressure and with the compression-coefficient of the liquid. It is known that, as a rule, dilution of a solution is accompanied by a decrease of volume. If no other causes were at work, the volume-change could be calculated from the known values of the osmotic pressure and the compression-coefficient. But the supposition which would be made in this calculation, viz., that the interior pressure (determined without reference to the osmotic pressure) is the same for different concentrations of a solution of the same substance, cannot be accepted as necessarily true, and there is no trustworthy method of calculation by which this point may be settled.

CHAPTER VI

DIFFUSION

1. **Generalities.**—Osmotic pressure is the cause of another class of phenomena, which come under notice when the pressure is allowed to exert itself freely. A movement of the particles of the dissolved substance occurs from the places where they are more closely packed, and where, therefore, they exert a greater pressure, to the places where they are present in smaller quantity, and where, therefore, the pressure is less; and this movement continues until the concentration, and therefore the pressure, is uniform throughout the liquid. The existence of this movement was discovered by Parrot;[1] the cause he called 'affinity of the first degree, a newly discovered natural force.' The phenomenon is now called diffusion; the cause has been shown recently, by W. Nernst,[2] to be osmotic pressure.

2. **Investigations of Graham.**—Graham was the first to make a thoroughgoing investigation of the phenomena of diffusion without a separating membrane.[3] His method of procedure was very simple. A wide-mouthed glass-jar, of about 200 grams capacity, with the upper edge of the mouth ground smooth, was filled with the salt solution under examination to within about 2 centims. of the top; water was then poured very carefully on to the top of the solution till the jar was quite full; the jar was placed in a

[1] *Gilb. Ann.* **51**, p. 318 [1815].
[2] *Zeitschr. f. physikal. Chemie*, **2**, p. 613 [1888].
[3] *Phil. Trans.* 1850, pp. 1, 805; 1851, p. 483.

glass cylinder, and water was poured into this cylinder until the jar was covered to the depth of about 3 centims.; about 1 litre of water was generally required. The whole arrangement was allowed to remain at rest for a considerable time in a moderately warm place. The process was stopped by covering the mouth of the jar with a glass plate; the jar was then removed from the outer vessel, and the quantity of the substance now present in the liquid in this vessel—the diffusate—was determined. The first result was that the quantity of the substance in the diffusate was largely dependent on the nature of the diffusing substance; acids, for example, diffused about twice as quickly as normal salts, and the rate of diffusion of these salts varied much according to their composition.

The quantity of substance which diffused from solutions of different concentrations was found to be nearly proportional to the contents of the original solutions; for instance, solutions of common salt which contained 1, 2, 3, and 4 parts NaCl in 100 parts water, yielded diffusates, after four days, which contained 2·78, 5·54, 8·37, and 11·11 grams salt—these numbers are in the proportion 1 : 1·99 : 3·01 : 4. The rate of diffusion was considerably modified by changes of temperature; thus a solution of common salt diffusing at 4·2° gave 10 grams NaCl in the diffusate, and at 19·4° the diffusate contained 13·6 grams NaCl, in each case after 8 days.

When two salts were allowed to diffuse simultaneously, each appeared to diffuse independently of the other. If, therefore, the rates of diffusion of the two salts were very different, it was possible to effect a fairly complete separation of the salts. For instance, a separation could be effected of the constituents of salts which were decomposed by water, e.g. potassium hydrogen sulphate, the alums, &c.; the details of this part of the investigation do not, however, concern us here.

The question with regard to the influence of salts on one another during diffusion was put into another form by

inquiring whether a salt diffuses in the solution of another salt in the same way as in pure water. Experiments showed no marked difference between the two cases. For instance, 9·06 grams Na_2CO_3 diffused in eight days from a 4 per cent. solution of this salt surrounded by pure water, and the quantities which diffused in the same time when the solution of Na_2CO_3 was placed in a 4 per cent. common salt solution were 8·82 and 9·1 grams. A slight retardation seemed to occur in some cases, but the results were not conclusive on this point.

I do not give in detail Graham's measurements of the relative quantities of salts which diffused under the same conditions, as the numbers are not of special importance for our purpose. Graham came to the conclusion that the quantities of chemically similar salts, such as potassium and ammonium chlorides, or potassium and ammonium nitrates, which diffuse in equal times are nearly, if not quite, equal. Such groups of salts as the sulphates or carbonates of the same base, showed agreements among themselves, but each group differed from those first mentioned.

3. **Fick's theory of diffusion.**—In order to gain an insight into the phenomena of diffusion, A. Fick[1] put forward, tentatively, the statement that, *the quantity of a salt which diffuses through a given area is proportional to the difference between the concentrations of two areas infinitely near one another.*

This fundamental supposition made by Fick follows, as a necessary consequence, from the statement, already made, that a substance in solution exerts a pressure proportional to the concentration of the solution. For the pressure exerted on both sides of the surface of separation between two adjacent portions of a solution is proportional to the concentration on each side; the resultant pressure must be proportional to the difference between the two concentrations, and it must drive the dissolved substance

[1] *Pogg.* **94**, p. 59 [1855].

towards the part of less concentration. This, however, is nothing else than the law stated by Fick.

The formal analogy between the statement of Fick and that made by Fourier concerning the conduction of heat, made it possible for Fick to carry over Fourier's theory of thermal conduction, which had been very carefully and fully developed by Fourier on mathematical lines of reasoning, and to apply it to diffusion-phenomena, by putting concentration in place of temperature, and quantity of salt in place of quantity of heat. The case wherein the process takes place only in one direction such that the same condition prevails at all points in a plane perpendicular to this direction, may be expressed by the differential equation :—

$$\frac{dy}{dt} = -k\left(\frac{d^2y}{dx^2} + \frac{1}{Q}\cdot\frac{dQ}{dx}\cdot\frac{dy}{dx}\right).$$

In this equation, x represents the distance in the direction of diffusion, y is the concentration, Q the area, and t the time; k = diffusion-constant, i.e. the number which expresses the quantity of salt diffusing through unit area in unit time when unit difference of concentration prevails throughout unit distance. The negative sign means that the diffusion occurs in the direction of smaller concentration. Should the area not depend on x, should, e.g., the diffusion-vessel be a prism or a cylinder, then $\frac{dQ}{dx} = 0$, and the equation is reduced to

$$\frac{dy}{dt} = -k\frac{d^2y}{dx^2}.$$

Finally, if a stationary condition is reached, i.e. if the concentration is maintained constantly equal in two parts of the diffusion-vessel, and sufficient time has elapsed, then the concentration is no longer dependent on the time; we have then $\frac{dy}{dt} = 0$, and therefore $k\frac{d^2y}{dx^2} = 0$; from this it follows that $\frac{dy}{dx} = a$, and $y = ax + b$, where a and b are

the integration-constants, which must be determined from the experimental conditions.

All these equations may be used for proving Fick's fundamental law, but one cannot obtain measurements of diffusion-constants by the help of this law. Fick's own measurements were applicable only to individual cases and were not very accurate, therefore I do not give them here. The researches of others have shown that to make accurate experiments on diffusion is one of the most difficult problems in practical physics.

4. **Experimental verification of the law of diffusion.**— Beilstein,[1] acting under the guidance of Jolly, sought to realise as simple a process of diffusion as possible, by the following arrangement. One limb of a U-shaped tube was cut off immediately above the bend, and the edge was ground flat; the longer limb was narrowed near the opening and was closed by a ground stopper. This arrangement was filled with the solution of a salt, fastened into a plate, and immersed in a vessel filled with pure water (fig. 19). This arrangement was chosen, as it was supposed that the dilution which resulted on diffusion would at once spread throughout the whole of the U-tube, because the dilute solution which formed at the open end of the tube, being specifically lighter, would find its way to the upper part of the tube, and would be replaced by the more concentrated solution originally present there. Beilstein supposed that an equal concentration would prevail throughout the whole of the little tube at each moment of the diffusion. This supposition does not, however, apply to the lower part of the bend at any rate, Nevertheless, if Beilstein's assumption is adopted as a first approximation, the

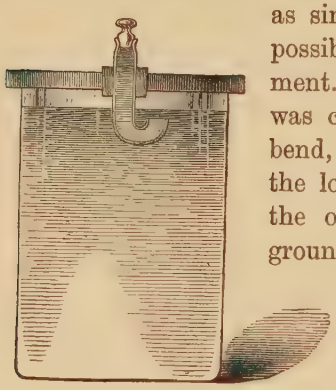


Fig. 19

[1] *Annalen*, **99**, p. 165 [1856].

process may be expressed on the basis of Fick's law. Putting y = concentration, i.e. the quantity of the salt for 1 gram of water in the little tube, then the rate of diffusion $\frac{dy}{dt}$ is proportional to the difference of concentration; but this difference is equal to the concentration itself, inasmuch as the exterior liquid is pure water, and because the diffusing salt-solution at once sinks to the bottom of the vessel and remains there during the experiment. We have, therefore,

$$\frac{dy}{dt} = -kcy$$

where k, as before, is the diffusion-constant, and c is a constant depending on the form, and especially on the area of the opening, of the vessel. It must be noticed in integrating, that for $t = 0$, the original concentration, which we shall call y_0, must be introduced; hence the equation follows—

$$ly_0 - ly = kct$$

where l expresses the natural logarithm.[1]

Beilstein found, for example, that a 2 per cent. solution of nitre contained 1·3052 per cent. after 24 hours, and ·8346 per cent. after 48 hours. The logarithms required are ·301 — 2, ·1155 — 2, and ·9215 — 3, and their differences are ·1855 and ·3795; these differences are in the ratio of 1 : 2·046, instead of 1 : 2. Similarly, a 4 per cent. solution of nitre (water = 100) gave 2·5437 per cent., and 1·6483 per cent., after 24 and 48 hours respectively; the differences of the logarithms are ·1966 and ·3852, and these are in the ratio 1 : 1·96. Beilstein examined 10 salts; he found that the second difference was a little smaller in almost every case than would be expected from the theory. He supposed himself driven to conclude that Fick's law is inaccurate; but Th. Simmler and H. Wild[2] at once pointed out that the

[1] The much more complicated equation given by Beilstein does not differ substantially from that given in the text.

[2] *Pogg.* **100**, p. 217 [1857].

deviations noticed might well have their origin in the somewhat inaccurate assumption which was made, that the contents of the small diffusion-vessel were perfectly uniform.

5. **Further investigations.**—In the contribution already referred to, Simmler and Wild put forward several methods for determining diffusion-constants, without, however, giving any experimental data. They integrate the differential equation for the case wherein a cylindrical diffusion-vessel, containing the solution of a salt, is sunk in water contained in a large vessel, and the quantity of salt which remains in the small vessel at the close of the experiment is estimated; also for the case in which two vessels of equal area and the same height are placed one over the other, the lower vessel being filled with the salt-solution and the upper with water. These authors also sketch a third method wherein they consider a prism-shaped vessel, and they propose to measure the concentration in each layer by determining the refraction-coefficient of the layer. They suggest that an insight might be had into the general process of the diffusion at any moment by producing a representation of the cord of a pendulum as seen through such a prism; the dislocations of the straight lines would afford measures of the concentrations of the different parts of the solution.

I do not note here the results of the calculations of Simmler and Wild, because those which are to be used later on will be recorded in their proper places.

Hoppe-Seyler,[1] and, independently and at the same time, E. Voit,[2] suggested and made use of an arrangement similar to the prism-method of Simmler and Wild. I shall give an account only of the last investigation, as it was of a systematic character. Equal volumes of a sugar solution and water were allowed to diffuse into one another in a vessel formed of mirror-plates and having the form of a parallelopiped; the amount of sugar was determined in

[1] *Med. chem. Untersuch.* Berlin, 1866.
[2] *Pogg.* **130**, pp. 227, 393 [1867].

each layer by a Duboscq-Soleil saccharimeter, which surrounded the diffusion-vessel, and was attached to the slider of a cathetometer-stand so that it could be fixed at different heights.

Simmler and Wild developed the following formula for a similar arrangement—

$$y = \frac{y_0}{2} + \frac{2y_0}{\pi} \sum_{p=0}^{p=\infty} \frac{(-1)_p}{2p+1} \cos \frac{2p+1}{\text{H}} \pi \text{ x.} e^{-\left(\frac{2p+1}{\text{H}}\pi\right)^2 k t}$$

y_0, as before, is the original concentration, y = concentration varying with the time t; H = height of the vessel; x = the height at which an observation was made, measured from above downwards; e = basis of the natural logarithms; $\pi = 3{\cdot}1415$; and p = any whole number from 0 to ∞. It is somewhat inconvenient to calculate k from this infinite series which quickly converges. By making observations at heights so that $x = \frac{1}{6}$ H and $x = \frac{5}{6}$ H, the second term, in which $p = 1$, becomes equal to zero, as under cos. the value $\frac{\pi}{2}$ or $\frac{5\pi}{2}$ appears. The third, and the following, term may be neglected without introducing any large error; so that we obtain for k the following closed expression:—

$$k = \frac{\text{H}^2}{\pi^2 t} \left\{ l \frac{2\sqrt{3}}{\pi} - l\left(1 - \frac{2y_1}{y_0}\right) \right\}$$

where y_1 represents the concentration measured at the height $\frac{1}{6}$ H, and at the time t. A simpler expression is found by combining two observations at the times t and $2t$. Putting y'_1 as the concentration at time t and the height $\frac{1}{6}$H, and putting $y_m = \frac{y_0}{2}$, it follows that

$$k = \frac{\text{H}^2}{\pi^2 t} l \frac{y_m - y_1}{y_m - y'_1}.$$

Calculations made by the use of this formula gave results which seemed to represent the diffusion-constants as

variable within the widest limits; the numbers for k varied between ·45 and ·16. Nevertheless, Voit was aware that this result need not lead to the conclusion that Fick's law is inaccurate. The result showed that the measurement of the amounts of sugar in different portions of a diffusing liquid by means of the saccharimeter is inadmissible; the values found were always much too low; and it was only after about 50 days, when the differences of concentration had been almost wholly equalised, that trustworthy measurements could be obtained. A description of the way by which Voit reached this conviction would lead us too far afield. Voit did not indicate an explanation of the divergent results he obtained. Such an explanation was found, in 1878, by Stefan,[1] who showed that a liquid whose refraction-coefficient decreases from beneath upwards, acts like a prism with the refracting edge upwards, and at the same time also acts as a cylindrical lens; a ray of light which enters such a liquid horizontally does not remain horizontal, but is bent aside. The diffusion-constants are therefore quite erroneous.

The investigations of Johannisjanz,[2] which were conducted in accordance with one of the optical methods suggested by Simmler and Wild, with certain appropriate changes, fall under the same criticism. As these investigations could not lead to accurate values, a description of them may be omitted.

6. **Investigations of H. F. Weber.**—None of the investigations which we have considered up to this point has led to trustworthy results. It is only within recent years that a research has appeared which has shown that the question concerning the validity of Fick's fundamental law of diffusion, which had remained unsolved for nearly a quarter-century, must be answered in the affirmative.

The problem has been solved by H. F. Weber,[3] by the help of a new principle of measurement. If two plates of

[1] *Wien. Sitzungsber.* **78.**
[2] *Wied. Ann.* **2**, p. 24 [1877].
[3] *Ibid.* **7**, pp. 469, 536 [1879]

zinc are immersed in two solutions of zinc sulphate, of different concentrations, connected by a porous partition or the like, an electromotive force is produced between the plates, and this force is proportional to the difference between the concentrations, provided that difference be small. Weber placed a concentrated solution of zinc sulphate in a cylindrical vessel, the bottom of which was formed of a smoothly amalgamated zinc plate; over this he poured a dilute solution of the same salt, and then, by a suitable arrangement, he fixed a zinc plate, similar to the first, beneath the surface of the upper layer of liquid. The electromotive force produced between the two plates measured the difference of concentration; as this difference became equalised by diffusion, the electromotive force decreased.

The application of Fick's law to this arrangement leads, as in all other cases, to infinite series, the coefficients of which may be caused partially to disappear by the use of suitable devices; if the times are made somewhat large, the remaining terms become numerically so unimportant that the first term suffices. Putting E as the electromotive force proportional to the difference of concentration, the course of the change of E, during the time of experiment, is given by the equation

$$E = A_e^{-\frac{\pi^2}{H^2} k t}$$

A is a constant, the other letters have the same meanings as before.

The testing of Fick's law was conducted by finding the values of $\frac{\pi^2}{H^2} k$ from the observations of the electromotive force on two consecutive days; this value must remain the same if the law is accurate. Weber found as follows:—

Days	Constant	Days	Constant
4–5	·2032	8–9	·2027
5–6	·2066	9–10	·2049
6–7	·2045	10–11	·2049
7–8	·2027		
			Mean ·2042

The constancy of the value is maintained in the most satisfactory way. *The diffusion-law of Fick is completely verified by these measurements.*

A modification of this method allows a more precise proof of Fick's law to be obtained, and at the same time makes it possible to complete the experiments in a few hours, which is a great advantage considering the necessity of keeping the temperature constant. Instead of obtaining two different conditions of concentration by placing different solutions one over the other, Weber gained the required arrangement by passing an electric current through a cell made of two amalgamated zinc plates placed horizontally and parallel to one another at a distance of ·5 centim. apart, and separated by a solution of zinc sulphate. The result of this arrangement is that some zinc is deposited on one side, and the solution surrounding this plate becomes more dilute, while the ion SO_4 travels to the other plate, dissolves some of the zinc, and so causes concentration of the liquid. At the same time there begins a process of diffusion which tends to equalise the difference of concentration; the final result is a stationary condition wherein the concentration increases regularly from one plate to the other. If the current is stopped, the cell shows an electromotive force corresponding with the difference of concentration which was produced in the first part of the experiment. This difference equalises itself by diffusion, and the process may be observed as before. The calculation leads to an expression the form of which completely corresponds with that already given, and which becomes sufficiently accurate after the expiry of a certain time.

Weber observed the electromotive force at equal intervals of time. The values must form a decreasing geometrical series, and the differences of their logarithms must be constant. The following table contains an example; the observations were all made at intervals of two minutes, and the differences of the logarithms are taken for those values which are separated by half-an-hour.

Time	E	Time	E	Diff. log.
h. m.		h. m.		
12 0	170·3	12 30	141·9	·07923
2	168·3	32	140·3	·07902
4	166·4	34	138·7	·07907
6	164·5	36	137·1	·07913
8	162·5	38	135·5	·07890
10	160·5	40	133·9	·07870
12	158·5	42	132·3	·07847
14	156·6	44	130·7	·07851
16	154·6	46	129·0	·07862
18	152·7	48	127·4	·07867

The small deviations shown by the differences are explained by the fact that the temperature fell somewhat during the observations. Temperature exerts a very marked influence on the diffusion-constant; while this has the value ·1252 at 1·2°, it becomes ·4146 at 44·7°; the general expression is $k = ·1187\ (1 + ·0557\ t)$.

Weber examined the influence of concentration on the diffusion-constant, by placing solutions of different strength between the plates. A small effect was discovered in the direction that the constant decreased slightly as concentration increased. A solution containing 21·4 per cent. gave $k = ·2403$, another solution of 31·8 per cent. gave $k = ·2289$. Weber concludes :—

> The elementary law of Fick is to be corrected in the same way in the theory of diffusion, as the elementary law of Fourier in the theory of the conduction of heat; as the magnitude of the internal heat-conduction decreases slowly as temperature increases, so the diffusion-values decrease gradually as concentration increases. Fick's hypothesis represents the process of diffusion with as great accuracy as Fourier's law expresses the process of the conduction of heat in solid substances.

This conclusion is evidently valid only on the supposition that the molecular condition of the dissolved substance is not changed by the dilution employed in the experiments. But it is certain that such changes occur with all solutions of salts, including zinc sulphate. Nevertheless, the

possibility remains that Fick's law is a completely accurate expression of the diffusion of substances which do not undergo changes of this kind.

7. **Graham's later researches and Stefan's calculations.**— Although the correctness of the diffusion-law and the limits within which it is valid were established by the decisive experiments of Weber, yet no general method for determining diffusion-constants was supplied by these experiments. Such a method is, however, given, as was pointed out by Stefan,[1] by an extended series of experiments published by Graham [2] in 1861. Graham used cylindrical vessels about 15 centim. high and 9 centim. wide; into these he poured ·7 litre water, and then allowed ·1 litre of the salt solution to flow under the water from a pipette with a very narrow orifice, so that the two liquids were plainly separated from each other. The vessels were then left at rest for a determinate time; 50 c.c. of the solution were then removed at a time, slowly and carefully, by means of a siphon, so that the whole liquid was obtained in 16 portions, and the analyses of these gave a survey of the diffusion-process.

Stefan applied the formal analogy between diffusion-movements and wave-motions to the calculation of Graham's results; both motions are expressed by the differential equation already quoted $\frac{dy}{dt} = -k\frac{d^2y}{dt^2}$. It is easy to integrate this equation for the case of an infinite cylinder; to apply it to a limited cylinder, Stefan made use of the principle of reflexion and superposition; he regarded the quantity of substance which would have passed beyond the limiting layer, if the liquid cylinder had been infinite, as totally reflected on to the limiting layer, and added to that present in the lower layers. If the curve *a b c* in Fig. 20, for instance, represents the falling off in the concentration of a diffusing system in a definite time, when the liquid cylinder is infinite, then the decrease in concentration, *a d*, in a cylinder which reaches only to the ordinate 5 is found

[1] *Wien. Akad. Ber.* 79, p. 161 [1879]. [2] *Phil. Trans.* 1861, p. 183.

by reflecting the part of the curve $b\,c$ as $b\,o$, and regarding the corresponding ordinates as applied to $a\,b$.

Stefan has calculated tables, by the help of which the distribution of the dissolved substance can be deduced, on the principle just stated, if the diffusion-constants are known; and by which also the diffusion-constants can be determined from the observed distribution of the substance.

For these and other calculations I must refer the student to the original memoir of Stefan; I do not give the tables, because it is very difficult to carry out investigations by the method under consideration without considerable errors. This becomes very apparent from the work of Schuhmeister,[1] wherein differences of from 10 to 20 per cent. appeared with-

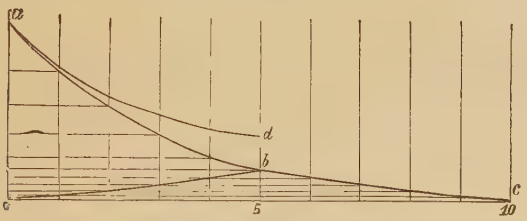


FIG. 20

out discoverable cause. Only the values of the constant k calculated from Graham's measurements are given here; the unit of length is the centimetre, and the unit of time is the day:—

	Temp.	k		Temp.	k
Caramel . . .	10°	·047	Sodium chloride . .	5°	·765
Albumin . . .	13	·063	„ „ . .	9	·910
Cane-sugar . .	9	·312	Hydrochloric acid .	5	1·742

8. **Investigations of Scheffer.**—Scheffer[2] used cylinders of 10 sq. centim. area, and about 10 centim. high; these were about two-thirds filled with the solution under examination, and one-third with water, and were then placed in a

[1] *Wien. Akad. Ber.* **79**, p. 603 [1879].
[2] *Berichte*, **15**, pp. 788 [1882]; **16**, p. 1903 [1883].

large vessel containing pure water. The calculations were made by the formula of Simmler and Wild (p. 125); a table is given of the values of the corresponding series. Observations made at different intervals of time gave results which agreed well with Fick's law. The values found for the constants (centim. days) were as follows:—

	Temp.	k		Temp.	k
Hydrochloric acid .	8°	2·13	Succinic acid . .	15°	·55
" " .	15·5	2·57	Citric " . .	9	·42
Oxalic " .	7·5	·70	Mannite . . .	10	·38
Acetic " .	8	·66	Sodium acetate . .	14·5	·69
" " .	14·5	·81	Chloral hydrate . .	9	·54
Tartaric " .	9	·43	Ammonium chloride .	17·5	1·31

The question of the influence of concentration on the diffusion-constants is discussed in a later communication. A distinct increase of the constant, as concentration increased, was noticed in the case of hydrochloric acid. No marked change was observed in the constants for sodium chloride and potassium chloride; and, lastly, the constants for sodium nitrate, sodium thiosulphate, and especially silver nitrate, became smaller as the concentration became greater.

At a later time,[1] Scheffer employed a somewhat different experimental arrangement. A stopper was ground into a cylindrical flask; the stopper carried a pipette with a stopcock, which reached to the bottom of the flask, and also an overflow-tube. Water amounting to three times the contents of the pipette was placed in the flask, the pipette was filled with the solution to be examined, and, by carefully opening the stopcock, this solution was allowed to flow in a layer under the water. When the experiment was finished, the liquid was caused to rise to the overflow-tube by carefully adding sufficient of the original solution, and the contents were withdrawn in four equal parts, three of which were used for analysis.

The results led to the conclusion that the diffusion-

[1] *Zeitschr. f. physikal. Chemie*, **2**, p. 390 [1888].

constant for hydrochloric acid increased considerably as concentration increased; in conformity with this, hydrochloric acid diffused into a dilute solution of the same acid much more rapidly than into pure water. Nitric and sulphuric acids showed the same behaviour, but in a much less marked way.

The tables on p. 134 contain a number of determinations made by Scheffer. The column n contains the quantities of water stated in molecules for one molecule of the dissolved substance; k = diffusion-constant.

9. **Diffusion in gelatinous substances.**—Graham[1] was the first to examine the question whether diffusion in water which has been gelatinised by such substances as starch, gum, or agar-agar, differs from diffusion in pure water. He came to the conclusion that the rate of diffusion of common salt is not appreciably altered by altering the condition of the medium.

F. Voigtländer,[2] as the result of an extended investigation, found that diffusion takes place in agar-agar in the same way as in pure water. This conclusion is of great importance for the measurement of diffusion-constants, as the chief causes of error—viz., differences of temperature and mixing caused by shaking—are here completely removed. For these reasons, also, the method gives a means of testing Fick's law with much greater sharpness.

For the case that concentration, c, remains constant at one end of an unlimited cylinder of water, Stefan calculated the quantity of a substance that diffused, a, as

$$a = c\,q\,\sqrt{\frac{k\,t}{\pi}}$$

where k = diffusion-constant, and q = area. The quantity diffusing through the given area must be proportional to the square root of the time. The following table shows the milligrams of sulphuric acid, a, that diffused from a solution of ·72 per cent. in t minutes, in a cylinder of agar-agar; the last column contains the quantities of sulphuric

[1] *Phil. Trans.* 1861, p. 183.

[2] *Zeitschr. f. bhysikal. Chemie*, 3, p. 316 [1889].

Temp.	n	k	Temp.	n	k
		Hydrochloric Acid, $HCl.nH_2O$.			
0°	5	2·31	11°	7·2	2·67
0	9·8	1·86	11	27·6	2·12
0	14	1·67	11	69·4	2·02
0	27·1	1·52	11	108·4	1·84
0	129·5	1·39			
		Nitric Acid, $HNO_3.nH_2O$.			
6	16·5	1·54	9	2·9	1·94
6	66	1·50	9	7·3	2·02
			9	35	1·78
			9	426	1·73
		Sulphuric Acid, $H_2SO_4.nH_2O$.			
7·5	686	1·04	8·5	127	0·99
8	18·8	1·07	9	686	1·14
8	36	1·01	11·3	71	1·12
8	84	1·02	13	0·5	1·3
			13	35	1·24
		Acetic Acid, $C_2H_4O_2.nH_2O$.			
8	38	0·66	13·5	60	0·76
13	46	0·73	13·5	84	0·77
13·3	208	0·78	14	128	0·81
3·5	315	0·61	13·5	1247	1·05
7·5	135	0·71	14	415	0·94
9·5	720	0·81	14	689	1·01
	Tartaric Acid, $C_4H_6O_6.nH_2O$.			Racemic Acid, $C_4H_6O_6.nH_2O$.	
5	155	0·37	5	155	0·39
	Potash, $KOH.nH_2O$			Soda, $NaOH.nH_2O$.	
13·6	1665	1·66	8	329	1·06
	Ammonia, $NH_3.nH_2O$.			Sodium Chloride, $NaCl.nH_2O$.	
4·5	16	1·06	5·5	11	0·73
4·5	85	1·06	5·5	25	0·74
			5·5	58	0·76
	Ammonium Chloride, $NH_4Cl.nH_2O$.			Barium Chloride, $BaCl_2.nH_2O$.	
17·5	61	1·31	8	337	0·65
	Silver Nitrate, $AgNO_3.nH_2O$			Sodium Nitrate, $NaNO_3.nH_2O$.	
6·5	10·6	0·57	2·5	7·7	0·57
7·5	11·8	0·65	2·5	44	0·62
7·5	25	0·77	11·5	28	0·82
7·5	189	0·90	11·5	95	0·86
	Urea, $CON_2H_4.nH_2O$.			Mannite.	
7·5	110	0·81	10	220	0·38

acid diffusing in 60 minutes calculated by the foregoing formula from the observed values of a :—

t	a	$\frac{a\sqrt{60}}{\sqrt{t}}$	t	a	$\frac{a\sqrt{60}}{\sqrt{t}}$
5	0·30	1·04	300	2·44	1·09
10	0·45	1·09	360	2·65	1·09
20	0·62	1·07	420	2·90	1·10
30	0·74	1·03	480	3·10	1·09
40	0·86	1·05	900	4·30	1·11
50	0·96	1·05	960	4·50	1·11
60	1·08	1·08	1020	4·61	1·10
120	1·48	1·05	1440	5·25	1·07
240	2·16	1·08	2880	7·05	1·02

The numbers in the last column evidently vary irregularly about a mean value. They decrease only towards the later experiments ; this is due to the fact that after two days the diffusion had reached the top of the cylinder, and therefore the formula was no longer valid.

Similar experiments were made with many other substances—salts, bases, and acids ; the conclusion was always the same ; the quantity that diffused was proportional to the square root of the time of diffusion.

The same law holds good for the distance over which a determinate concentration extends ; this also is proportional to the square root of the time of diffusion. That concentration of an acid which was required to decolorise the jelly, which had been coloured red by extremely dilute alkaline phenolphtaleïn, was adopted as the characteristic concentration. The progress of the decolorising action was found to be exactly proportional to the square root of the time. The same result was obtained for the reddening of the jelly containing phenolphtaleïn by diffusing alkalis.

Finally, Voigtländer determined a number of diffusion-constants in terms of the usual units (centimetres and days). The results obtained may be taken as valid for water also ; for measurements made with jellies containing from 1 to 4 per cent. of gelatinising substance showed, under the same conditions, exactly the same quantities of

diffused acid, so that the supposition that the presence of agar-agar is without influence on the diffusion seemed to be justified. The numbers obtained in this investigation are more accurate than those furnished by experiments with water by reason of the complete absence of disturbing currents.

The influence of temperature was examined at the same time. The following table contains the results; fairly dilute solutions were generally used; the temperature-coefficients of the diffusion-constants are given under a_1 and a_2; a_1 holds good for 0° to 20°, a_2 from 20° to 40°. The experiments showed that the quantities diffusing in equal times increased very nearly in proportion to the temperature. From this, taken in conjunction with the formula on p. 133 which shows that the diffusion-constant increases in proportion to the square root of the quantity of substance, it follows that the temperature-coefficient in each case takes the form $k_t = k_0 (1 + \beta t)^2$.

	k_0	k_{20}	k_{40}	a_1	a_2
Formic acid	0·472	0·867	1·49	·0228	·0306
Acetic „	0·318	0·64	1·04	·0245	·0326
Propionic „	0·245	0·514	0·882	·0261	·0358
Butyric „	0·217	0·443	0·788	·0256	·0385
Oxalic „	0·461	0·894	1·47	·0242	·0322
Tartaric „	0·316	—	0·996	—	—
Citric „	0·231	—	0·854	—	—
Sulphuric „	0·637	1·21	2·01	·0236	·033
Hydrochloric acid	1·07	2·06	—	·0246	—
Nitric „	1·10	2·10	—	·0226	—
Potassium oxide	1·01	1·75	2·36	·0209	·026
Sodium „	0·764	1·26	1·35	·0195	·024
Ammonium	0·661	1·26	—	·023	—
Lithium oxide	0·591	1·13	1·81	·0239	·0295
Barium „	0·735	1·33	2·10	·0224	·0291
Strontium „	0·685	1·26	2·01	·0229	·0297
Calcium „	0·735	1·40	2·18	·0237	·028
Potassium chloride	0·786	1·40	2·18	·0219	·0279
Sodium „	0·535	1·04	1·71	·0243	·0332
Ammonium „	0·682	1·32	2·16	·0236	·0314
Calcium „	0·394	—	1·40	—	—
Magnesium „	0·402	0·77	1·40	·024	·0346
Barium „	0·525	0·98	1·58	·0232	·0306
Nickel „	0·454	0·84	1·48	·0231	·0322
Cobalt „	0·443	0·83	1·33	·0232	·0304

10. Investigations of Long.—By the use of a special arrangement proposed by L. Meyer, J. H. Long[1] made direct determinations of the diffusion-constants of a series of salts, without the employment of any complicated formulæ such as had been required by all previous investigators. The method, it is true, gave only relative numbers. The chief part of the apparatus (fig. 21) consisted of a tube bent several times, carrying a funnel at one end and having in the middle a short piece open beneath (fig. 21, *i*), and ending in a somewhat narrow orifice. The tube was hung in a beaker which contained the salt-solution. A slow stream of water was poured at a uniform rate into the tube by means of the funnel; this stream of water washed the tube and then glided quietly over the salt-solution, the even

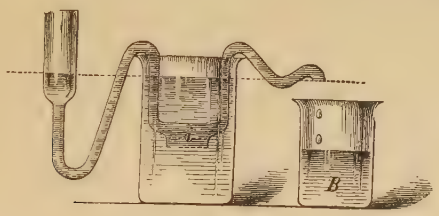


FIG. 21

surface of which reached some way into the short open piece (to about *i* in fig. 21). Diffusion took place at this surface; now, inasmuch as the water was being constantly renewed in the tube, and the quantity of solution in the beaker was considerable, it might be assumed that diffusion was taking place between two liquids of unchanging composition. Under these conditions the quantity of salt which diffused through the surface *i* and was carried by the stream of water into the vessel B must have been proportional to the concentration, the time, and the diffusion-constant. Long did not reduce his results to absolute units, but gave the quantity of salt which diffused through the surface *i*, the diameter of which was 1·45 centims., in one

[1] *Wied. Ann.* **9**, p. 613 [1880].

day. The length of the short piece was 1·1 centim. The solutions used contained one equivalent, or a fraction of one equivalent, of each salt in one litre. Preliminary experiments showed that the diffusion proceeded very nearly in proportion to the concentration. The following table gives the quantities which diffused in one day from normal solutions. The corresponding values from Graham's first series of experiments are also given; these numbers were calculated by Long by finding, with the help of Fick's formula, the quantity of salt which would diffuse from one of Graham's flasks had the diameter of the neck been 1·45 centims., the actual diameter being 3·048 centims. The length of the neck of Graham's flasks was nearly the same as that of the short piece of glass used by Long. The two series of numbers show a general agreement. Nevertheless some of the differences are not small; this is doubtless due to the fact that the arrangement of Graham's experiments did not lend itself well to the method of calculation used by Long.

	Long	Graham		Long	Graham
KCl	·0599	·0638	$CoCl_2$	·0397	—
NaCl	·0351	·0373	$NiCl_2$	·0394	—
NH_4Cl	·0369	·0378	KBr	·0965	·1037
LiCl	·0233	—	NaBr	·0525	·0645
$CaCl_2$	·0476	·0547	NH_4Br	·0617	—
$SrCl_2$	·0686	·0766	KI	·1364	·1416
$BaCl_2$	·0936	·0974	NaI	·1008	·0959
$MgCl_2$	·0373	·0444	KCy	·0499	—
KNO_3	·0614	·0715	$\frac{1}{2}CuSO_4$	·0252	·0235
NH_4NO_3	·0544	·0596	$\frac{1}{2}ZnSO_4$	·0269	·0194
$NaNO_3$	·0446	·0531	$\frac{1}{2}MnSO_4$	·0226	—
$LiNO_3$	·0353	—	$\frac{1}{2}MgSO_4$	·0209	·0150
$\frac{1}{4}BaN_2O_6$	·0429	·0296	$\frac{1}{2}Na_2SO_4$	·0478	·0300
$\frac{1}{4}SrN_2O_6$	·0249	·0241	$\frac{1}{2}(NH_4)_2SO_4$	·0482	·0369

To bring out more clearly the stoïchiometrical relations of the values obtained, Long divided the numbers in the foregoing table by the molecular weights of the different salts. The results show how many molecules diffuse under equal conditions. The values are :—

	Cl	Br	I	NO_3	SO_4
K . .	803	811	823	607	—
Na . .	600	509	680	512	678
NH_4 . .	689	629	672	524	724
Li . .	541	—	—	512	—
Ba . .	450	—	—	656	—
Sr . .	430	—	—	552	—
Ca . .	429	—	—	—	—
Mg . .	392	—	—	—	348
Zn . .	—	—	—	—	332
Mn . .	—	—	—	—	298
Co . .	306	—	—	—	—
Ni . .	304	—	—	—	—
Cu . .	—	—	—	—	316

This table shows a somewhat regular arrangement of the molecular diffusion-values. The haloid compounds of potassium, as also those of sodium and ammonium, agree among themselves; the sulphates of the magnesium group have also approximately equal values. By making a comparison with other properties, a very near parallelism is noticeable between the rates of diffusion and the electrical conductivities of substances.[1]

11. **Simultaneous diffusion of mixed substances.**—In his first series of experiments, Graham announced that mixed substances diffuse almost independently of one another, each at its own specific rate; and in his second communication he showed how this behaviour may be employed to separate mixed substances, inasmuch as that which diffuses more rapidly collects in the upper part of the diffusion-vessel, while the other remains behind. For example, a solution containing 5 per cent. NaCl and 5 per cent. Na_2SO_4 gave an upper layer, 90·6 per cent. of the salt in which consisted of sodium chloride.

A systematic investigation of this question was conducted by C. Marignac[2] in 1874. The object of this research was to estimate the relative diffusion-coefficients

[1] This relation is more closely examined in a later chapter of the author's *Lehrbuch.—Translator.*

[2] *Ann. Chim. Phys.* (5), **2**, p. 546.

of two salts from measurements of the simultaneous diffusion of the salts. The most considerable sources of error—currents caused by local differences of temperature, agitation of the liquid, &c.—affect both parts equally, so that they more or less disappear when the results are compared. Unfortunately, no general relation could be traced between the rates of diffusion of the single salts and the mixture, except perhaps that the rate of diffusion of the salt which diffused more rapidly seemed to be increased.

The arrangement of Marignac's experiments was similar to that formerly adopted by Graham; the solutions were contained in wide-mouthed small glasses, which were placed in larger vessels containing water and having a capacity about 10 times that of the smaller glasses.

Marignac tried to use the formula of Beilstein (p. 123) for calculating the results; but the values thus obtained, as was to be expected, varied according to the duration of the experiments. Marignac then substituted an empirical formula,[1] putting in place of $k = \log. y_0 - \log. (y_0 - y)$ the expression $k = \log. y_0 - \log. (y_0 - 2y)$, and thus obtaining the following formula for the proportion of the diffusion-constants of two salts:—

$$\frac{k}{k'} = \frac{\log. y_0 - \log. (y_0 - 2y)}{\log. y'_0 - \log. (y'_0 - 2y')}.$$

The following table shows the applicability of this formula; the column headed I. contains the direct proportion of the two salts in the diffusate, II. contains the ratio of the diffusion-coefficients calculated by the formula of Beilstein, and III. contains the same ratio calculated by Marignac's formula. The two salts, potassium chloride and potassium sulphate, were present in equal quantities. The numbers in column III. are to some extent constant.

[1] The salt which diffuses out is here represented by y; as Beilstein used y to represent the salt which remained behind, Beilstein's y must be replaced by Marignac's $y_0 - y$.

Weight of each salt	Weight of water	Time in days	I.	II.	III.
2·5	50	7	·460	·439	·415
1·7	34	8	·494	·465	·426
1·8	36	10	·537	·488	·409
1·7	34	11	·556	·513	·427
2·7	54	12	·519	·478	·415

Marignac also examined the question whether the proportion of the quantities of the two salts influenced the ratio of their diffusion-constants. The table which follows gives information on this point, and also on the influence of dilution; the diffusing salts are $BaCl_2$ and NaCl, and the diffusion-coefficient of NaCl is taken as unity.

Salt-contents in 100 Parts of Water

$BaCl_2$: NaCl	20	15	12·5	10	7·5	6·25	5	3·75	2·5
1 : 4	—	—	·605	—	—	·621	—	—	—
1 : 2	—	·629	—	—	·623	—	—	·645	—
1 : 1	·670	—	—	·654	—	—	·653	—	·653
2 : 1	—	·630	—	—	·666	—	—	—	—
4 : 1	—	—	·649	—	—	·659	—	—	—

The influence of dilution is seen to be very small. A change in the proportion of the two salts affects the diffusion in the way that the salt which is present in larger quantity diffuses in advance of the other to a greater extent than corresponds with its quantity. This means, in general terms, that the salt which diffuses more rapidly is somewhat accelerated by the presence of the other salt, while the more slowly diffusing salt is much delayed. The differences are not great even for very large changes of the proportion between the salts, only amounting to about 6 per cent. for a change of 1 : 16; they may therefore be neglected in a first approximation.

In other cases, however, dilution exerts a very marked effect. Three cases may be distinguished, for which the following rules hold good with certain exceptions.

1. The proportion of the diffusion-coefficients (the

greater is always taken as = 1) increases with increasing dilution. This is the most common case; it holds good, for example, for those salts which contain the same metal.

2. The proportion is unchanged. This case occurs most commonly for salts of the same acid, seldom for a mixture of salts of the same metal.

3. The proportion decreases with increasing dilution. This case seldom occurs.

In order to obviate as far as possible the changeable effect of dilution, dilute solutions containing 1·25 per cent. of the salt were generally employed.

In accordance with the plan described above, Marignac allowed five pairs of salts to diffuse singly and also together, in order to arrive at the ratio of the diffusion-coefficients from the ratio of the quantities of salts which diffused simultaneously. In the following table, r signifies the ratio of the diffusion-coefficients when the salts diffused separately, r' = the same ratio when the salts diffused together, $r' : r$ = the ratio of these two ratios, and R = the ratio between the quantities of the same salt when diffusing with the other salt and when diffusing alone, and, therefore, the change in the diffusion-coefficient brought about by the presence of the other salt.

	Separately	Together	r	r'	$r : r'$	R
NaCl	·5833	·6054	1	1	—	1·038
Na_2SO_4	·3770	·2497	0·590	0·352	·596	0·662
KCl	·8560	·9276	1	1	—	1·083
$BaCl_2$	·8433	·4424	0·572	0·401	·701	0·814
NaCl	·7142	·7883	1	1	—	1·019
$BaCl_2$	·5673	·5225	0·757	0·668	·882	0·921
K_2SO_4	·4745	·4378	1	1	—	0·901
$MgSO_4$	·2028	·1684	0·382	0·345	·903	0·830
Na_2SO_4	·3757	·3420	1	1	—	0·910
$MgSO_4$	·2097	·1823	0·523	0·502	·960	0·869

The proportion of the diffusion-coefficients determined by the simultaneous diffusion of the salts, r', is always a little smaller than that determined by separate diffusion; $r' : r$ is therefore always less than unity. The numbers

in column R show that the cause of this is to be found in the hastening of the diffusion of the more quickly diffusing salt, and the retardation of the diffusion of the more slowly diffusing salt; in the two last combinations in the table both salts are retarded, but the more slowly diffusing salt is retarded more than the other. When the salts diffuse together they are separated from one another more completely, in reference to their rates of diffusion, than when they diffuse separately.

I cannot give the whole of Marignac's very numerous measurements of the simultaneous diffusion of pairs of salts. But I append a series of tables which show the ratios of the diffusion-coefficients of various salts; the numbers refer to 1·22 grams of salt in 100 grams of water; the diffusion-coefficient of the salt at the head of each column is taken as unity.

Potassium Salts

	Nitrate	Carbonate	Sulphate
Chloride	1·081	2·369	1·919
Bromide	1·091	2·267	—
Iodide	1·112	2·267	—
Permanganate	·880	—	—
Fluoride	·768 [1]	—	—
Chromate	·621	1·295	—
Sulphate	·651	1·135	—
Carbonate	·494	—	—
Perchlorate	—	1·872 [2]	1·486 [2]
Chlorate	—	1·862	1·464

Chlorides

	Sodium	Potassium
Potassium	1·518	—
Ammonium	1·175	·849
Calcium	·669	—
Barium	·653	·428
Mercury	·651	—
Strontium	·637	—
Magnesium	·557	—
Hydrogen	—	3·389

[1] 5 per cent. salt.

[2] ·9 per cent. salt.

NITRATES

	Potassium	Sodium
Hydrogen	3·649	—
Ammonium	1·000	—
Potassium	—	1·543
Silver	—	1·197
Lead	—	·681
Calcium	—	·674
Strontium	—	·666
Magnesium	—	·632

SULPHATES

	Potassium	Sodium	Magnesium	Manganese
Hydrogen	2·101	—	—	—
Potassium	—	1·437	—	—
Ammonium	·973	—	—	—
Manganese	—	·533	—	—
Magnesium	·386	·531	—	·971
Zinc	—	·492	·801	—
Copper	—	·475	—	—
Aluminium	·285	—	—	—

The most important result to be drawn from the numbers in these tables is that the rates of diffusion of the acids are related to those of the metals so that all the salts of any specified acid always follow in the same order, whatever the acid may be, and so also, all the salts of any metal follow in the same order, independently of the nature of the metal. The following table may be constructed to show the order of the diffusion-coefficients:—

Cl, Br, I	H
NO_3	K, NH_4
ClO_3, ClO_4, MnO_4	Ag
F	Na
CrO_4	Ca, Sr, Ba, Pb, Hg
SO_4	Mn, Mg, Zn
CO_3	Cu
	Al

This table exhibits a great resemblance with a corresponding table showing the conductivities of salt-solutions.[1]

[1] These conductivities are fully discussed in a later chapter of Ostwald's *Lehrbuch.—Translator.*

12. Theory of the phenomena of diffusion.—It has been pointed out already that we must regard the osmotic pressure of the dissolved substance as the impelling force in the phenomena of diffusion. As osmotic pressure is proportional to concentration, it follows at once that the rate of diffusion, which is conditioned by the difference between the osmotic pressures in two adjacent layers, must also be proportional to the difference of the concentrations, as it is stated to be in Fick's fundamental law. W. Nernst[1] was the first to attribute the phenomena of diffusion to the osmotic pressure; the following method of calculation is due to him.

In a diffusion-cylinder of area q let a portion, x, be measured off along the axis, and let the osmotic pressure in this portion be p. Then the pressure of the quantity of substance in the cross-layer $q\,d\,x$ is $-q\,dp$. If c is the concentration, i.e. the quantity of substance in gram-molecular weights in unit-volume (1 c.c.), then the quantity of substance in the layer $q\,d\,x$ is $c\,q\,d\,x$, and therefore the total pressure on 1 gram-molecular weight is $-\frac{q\,dp}{c\,q\,d\,x} = -\frac{1}{c}\cdot\frac{dp}{dx}$. Let κ be the force which communicates a velocity of 1 centim. per second to 1 gram-molecule of the substance in solution. Then putting s as the quantity of substance, measured in gram-molecules, which passes through the area q, by reason of the difference of pressure, $d\,p$, in the time z, the value of s is given by the equation

$$s = -\frac{q\,z\,d\,p}{\kappa\,d\,x}.$$

If p_0 is the pressure in a solution of unit concentration, then $p = p_0\,c$, and therefore

$$s = -\frac{q\,z\,p_0}{\kappa}\cdot\frac{d\,c}{d\,x}.$$

[1] *Zeitschr. f. physikal. Chemie*, **2**, p. 613 [1888].

Fick's law takes the form

$$s = -kqz\frac{dc}{dx},$$

from which it follows that

$$k = \frac{p_0}{\kappa}.$$

As the diffusion-coefficient is generally referred to one day as the unit of time, it must be divided by 86,400 to reduce it to the second as the unit. Therefore

$$\frac{k}{86400} = \frac{p_0}{\kappa}.$$

The pressure p_0 is obtained from the volume occupied by 1 gram-molecule of oxygen, i.e. 32 grams, at 0° and 760 mm. pressure; this volume is 22,376 c.c. To compress this gas at $t°$ to the space of 1 c.c. a pressure of $p_0 = 22{,}376\ (1 + a\,t)$ must be used. The fact that Boyle's law does not hold good at such pressures as this is of no importance here, as we are concerned with it only for the purpose of calculation.

Remembering that 1 atmosphere is equal to a weight of 1·033 kilo., we obtain the following expression for the force in round numbers :—

$$\kappa = \frac{2 \times 10^9\ (1 + a\,t)}{k} \text{ kilos.}$$

Substituting the experimentally determined value of k, we obtain the force which acts on 1 gram-molecule. For instance, Scheffer found $k = \cdot 81$ for urea at 7·5°; hence $\kappa = 2{\cdot}5 \times 10^9$ kilos.

The force which must be used to drive 1 gram-molecule—60 grams—of urea ($CO.N_2H_4 = 60$) through water with a velocity of 1 centim. per second has the enormous value of 2,500 million kilograms. The cause of the enormous friction which opposes the movement of the molecules is to be sought for in the very great number of the molecules. When a mineral is ground to fine dust, we

know that the force of gravity, which communicates to the whole piece a velocity of 980 centims. per second, does not now produce a velocity of more than, say, 1 centim., because of the friction of the air. To cause the former velocity it is necessary to employ a force equivalent to ten thousand times the weight of the dust, assuming that the velocity increases in proportion to the force. It is thus easy to conceive how enormously the friction to be overcome must increase in the case of a division so great as that into individual molecules, especially when it is remembered that the friction of the medium (water) is very great.

The foregoing discussion applies to substances which remain undivided when dissolved. It will be shown hereafter that this provision does not apply to salts. The theory of the diffusion of salts is therefore much more complicated than that of the diffusion of indifferent substances. It is especially to be noted that electrical forces come into play in the diffusion of salts, or, speaking generally, of electrolytes; the corresponding theory will therefore find its proper place in a later chapter.[1] Mention must, however, be made here of the fact that Fick's law can be deduced from the corresponding observations made with salts in very dilute solutions, so that the experimentally proved applicability of the law is there also in unison with the theory now developed.

Finally, the question regarding the nature of osmotic pressure, which is the cause of the phenomena of diffusion, is to be answered by looking to the kinetic energy of the molecules of the dissolved substances, just as the cause of the pressure of gases, with which osmotic pressure corresponds in its numerical relations and in all other relations expressible by general laws, is sought for in the kinetic energy of the gaseous molecules. For, as the molecules of the solvent in the interior of the solution act equally in all

[1] This subject is discussed in the second volume of the *Lehrbuch*.—*Translator.*

directions on each molecule of the dissolved substance, these molecules are all free to move as if there were, on the whole, no action upon them. Hence it follows that the kinetic energy of the molecules of the dissolved substance is equal to that of the gas at the same temperature; and, moreover, as the kinetic energies of the molecules of the dissolved substance and of the solvent must agree, because these molecules are in immediate contact, it follows also that the kinetic energy of the molecules of the liquid must, on the whole, be the same as that of gaseous molecules at the same temperature.

The question concerning the hypothetical exposition of the cause of osmotic pressure is, however, of little importance at present. The development of the conclusions which follow from the fact of this pressure, and from the knowledge of its numerical laws, has already furnished such a multitude of important results, and now points the way to so many more of equal importance, that the need of a hypothetical exposition of the cause of the pressure has not been felt. Such a need would arise only if the immediate consequences were exhausted, and if a vantage-point for further advance were to be gained by a special hypothetical treatment of the fundamental facts. But we are as yet far from this position.

13. **Homogeneousness of solutions.**—Should adjacent portions of a solution be of different concentrations, then, inasmuch as the osmotic pressure acts throughout, an impulsion of the little particles of the dissolved substance must take place in the direction of equalising the differences of concentration, and this must continue until the solution has become completely homogeneous. Agreeably with this statement, experience tells that the dissolved substance is always found perfectly equally distributed in any solution, after some time.

The question has sometimes been mooted whether 'the specifically heavier salt-particles' might not be expected to show a tendency to gather together in the lower part of the

solution under the influence of gravity. This supposition was made more especially by Beudant,[1] on the ground that crystals were found to have separated at the bottom of a flask containing an unsaturated solution which had been set aside in a cupboard. Gay-Lussac, however, found that no separation of solid occurred from salt solutions in tubes 1 m. long after standing for six months in the cellars of the Paris Observatory;[2] the under layers had exactly the same composition as the upper layers. At a later time doubt was thrown on this result by Bischof, but the experiments which he brought forward were not free from objection.[3] Lieben[4] showed, somewhat later, that no separation occurs either with solutions of solids or of gases. It is therefore certain that homogeneous solutions are not changed to a measurable extent by the action of gravity. Gouy and Chaperon[5] have examined the same question recently, using a thermodynamic method. Their reasoning cannot be given here; the result is that gravity has no influence on the contents of the solution, provided the density is not changed by a small change of concentration. If the solution becomes denser with increasing concentration the lower layers become more concentrated, and *vice versâ*; the first case is much the more common. The amount of action is very small; the following numbers represent the approximate values, by calculation, of the differences between the uppermost and undermost layers of various salt-solutions in tubes 100 m. long:—

Substance	Under layer	Upper layer	Difference
Solution of cadmium iodide . .	·166	·153	·013
„ sodium acetate . .	·200	·196	·004
„ „ chloride . .	·110	·1095	·0005
„ sugar	·550	·546	·004

[1] *Ann. Chim. Phys.* (2) **8**, p. 15 [1819]. [2] *Ibid.* **11**, p. 306 [1819].
[3] *Lehrbuch der Chem. und phys. Geol.* **2**, p. 1712.
[4] *Annalen*, **101**, p. 77 [1857].
[5] *Ann. Chim. Phys.* (6) **12**, p. 384 [1887].

The differences are so small that their experimental demonstration is hardly practicable.

The case is different when the parts of a homogeneous liquid are at different temperatures; a change in the distribution of the dissolved substance occurs, in the direction that the solution becomes more concentrated in the colder than in the warmer part. This fact was made certain for the first time by C. Ludwig.[1] After him K. Möller thought he had found a change under similar conditions but in the opposite direction. Finally Ch. Soret[2] made a more thorough examination of the subject. The upper part of a tube filled with a salt-solution was maintained at 80°, and the under part at 20°; after 50 to 56 days the contents per 100 parts were as follows :—

Potassium Chloride

Warm	Cold	Ratio
23·19	24·89	·0682
16·71	17·94	·0684
11·85	12·52	·0541
9·83	10·54	·0679

The numbers headed 'ratio' express the differences between the contents of the two parts of the solution divided by the contents of the colder part. The ratio is constant, except in the third experiment where there is probably an experimental error. Similar results were obtained with solutions of sodium chloride, lithium chloride, and nitre; the dissolved salt was always concentrated in the colder portion of the solution.

The theory of these phenomena was pointed out by van 't Hoff.[3] As the osmotic pressure increases in proportion to the absolute temperature, diffusion must occur in Soret's experiments from the warmer to the colder parts until the osmotic pressure has become the same in both

[1] *Wien. Akad. Ber.* **20**, p. 539 [1856].
[2] *Ann. Chim. Phys.* (5) **22**, p. 293 [1881].
[3] *Zeitschr. f. physikal. Chemie*, **1**, p. 487 [1887].

parts, and therefore the concentration must vary inversely as the absolute temperature. The absolute temperature of the lower part was $273+20=293°$, and that of the upper part was 353°; the ratio of these numbers is 1·205; the ratio of the concentrations, 1·068, was found to be three times smaller. The conclusion is that the diffusion in the long tube had not completed the process of separation. It is also to be noted that the concentration was not determined at points of constant temperature, but the whole solution was divided into two parts; this would of course have the effect of decreasing the differences. The results of observations with copper sulphate agreed much better with the theory. These were as follow :—

Warm	Cold	Ratio
14·04	17·33	1·234
23·87	29·87	1·252

The ratio found by experiment is here greater than that deduced theoretically (1·205), but the applicability of the theory is somewhat doubtful by reason of the great concentrations. The question certainly deserves a thorough experimental examination.

14. **Crystalloids and colloids.**—In one of his communications, which has been already referred to, Graham pointed out the very marked differences that are noticeable in the rates of movement of different substances through water. The free acids and bases come first in order, and they are followed closely by the neutral salts. There are, however, a number of substances the diffusion of which is very much slower; examples of these substances are furnished by gums, tannin, albumin, and caramel. The annexed table shows approximately the times required for the equal diffusion of the various substances named :—

Hydrochloric acid	1	Magnesium sulphate	7
Sodium chloride	2·33	Egg albumin	49
Sugar	7	Caramel	48

The two groups of substances which differ so much as regards diffusion differ also in other respects. Those which diffuse rapidly are generally known in the crystalline form, whereas the others are amorphous. Those of the first group dissolve in water with more or less marked changes of temperature; they raise the boiling-points, lower the freezing-points, and generally exert a marked influence on the properties, of their solutions. The others do not exhibit all these properties: their solutions are mechanical mixtures rather than compounds. Graham distinguished these two classes by the names *crystalloids* and *colloids*.

Colloidal substances are able to exist in two modifications, the soluble and the coagulated or pectinised. The change from the soluble to the pectinised form generally occurs spontaneously by lapse of time; in most cases it may be produced by the addition of certain substances which do not seem often to exert any definite chemical action.

Silicic acid, alumina, ferric oxide, &c., are among the substances which may be obtained in the colloidal form; the details concerning these substances do not concern us here.

The most important property of colloids, as regards our present subject, is that *they oppose no marked hindrance to the diffusion of crystalloids, but they are more or less impermeable by other colloids*. If, therefore, a mixture of crystalloidal and colloidal substances is cut off from pure water by a colloidal membrane of a different kind, the crystalloids will diffuse into the water, but the whole of the colloids will remain behind. Graham applied the term *dialysis* to processes of this kind. Very different substances may be used as the colloidal separating membrane; animal bladder and parchment-paper are the most convenient.

We may look on separating colloidal membranes as those the interstices of which are large enough to allow the passage of the smaller molecules of crystalloids, while they stop the passage of the larger molecules of colloids.

15. **Osmosis.**—It has been remarked at the beginning of the last chapter that the phenomena of diffusion which appear when a porous membrane is present attracted attention and were investigated much earlier than the simpler phenomena of free diffusion. Dutrochet tried to measure this kind of diffusion; he covered a small glass, which was furnished with a long neck, with a bladder, poured in a liquid, and placed this 'osmometer' in the other liquid. The height to which the inner liquid rose was regarded by Dutrochet as a measure of the 'osmotic force.' It is evident that this arrangement could not lead to accurate measurements, for the phenomena which it was wished to examine were interfered with irregularly by the filtration of the liquid under the pressure of the raised column.

Vierordt constructed an apparatus with a membrane placed vertically and with an invariable pressure.

The earlier experimenters who busied themselves with the phenomena of diffusion through membranes were aware that there are two streams setting in opposite directions through the separating membrane, and that these continue until complete equality has been established. Jolly [1] investigated the question whether a definite relation prevails between the quantities of the substances which pass through the membrane in different directions; he arrived at the conclusion that for each quantity of substance (e.g. a salt) which passes out, a proportionate quantity of the exterior liquid (e.g. water) passes in.

Jolly said that if a tube is closed by a piece of bladder, a specified quantity, about 2·4 grams, of common salt is placed inside, and the whole is suspended in water which is frequently removed, water collects in the interior of the tube, and the quantity of water increases until it becomes 10·36 grams, after which it remains constant. In this experiment 2·4 grams of common salt are replaced by 10·36 grams of water, or 1 gram by 4·32 grams of water. The same result was obtained if an indeterminate quantity of water

[1] *Pogg.* **78**, p. 261 [1849].

was added to the salt at the beginning of the experiment, or if a solution of the salt was used; the water which was present at first behaved indifferently, and 4·3 grams more water entered for every 1 gram of common salt which passed outwards. The quantity of water which thus replaced sodium chloride—the 'osmotic equivalent'—was calculated by Jolly from different experiments to be 4·32, 4·58, 3·99, 3·82, 4·35, 4·09. Jolly conducted similar experiments with the sulphates of sodium, potassium, magnesium, and copper, also with acid potassium sulphate, sulphuric acid, potash, alcohol, sugar, and gum.

Jolly's conclusions were soon contradicted. C. Ludwig[1] repeated the experiments, but he failed to find any 'osmotic equivalents'; he found, on the contrary, that the proportion of the quantities of salt which passed out to the water which passed in depended very notably on the original concentration. The direction of this dependence varied for different salts; for instance, the 'osmotic equivalent' of Glauber's salt was greater the more dilute the solution, while for common salt the 'equivalent' decreased as dilution increased.

C. Eckard[2] examined this question more thoroughly He showed that the 'osmotic equivalent' depends on the nature and the condition of the membrane. This observation removed the problem entirely to the domain of physiology; since Eckard's work it has been considered almost wholly from that standpoint.

The processes which take place with membranes of the nature of animal bladders stand midway between the purely osmotic phenomena which were described in the preceding chapter and those of pure diffusion. They approach osmotic processes in so far as the membrane hinders the outflow of the dissolved substance. But this hindrance is not complete; the movement of the substance through the membrane is only very much lessened in proportion to that of the water; it is by no means stopped. An osmotic rise

[1] *Pogg.* **78**, p. 307 [1849]. [2] *Ibid.* **128**, p. 61 [1866].

of pressure results, but does not reach its proper value. At the same time a diffusion through the membrane takes place, but much more slowly than in water; the contents of the 'osmometer' are thus diluted continuously until the movement stops. It is evident, then, that the properties of the membrane play a decisive part, and that the phenomena are therefore removed from the class of events which concern us at present.

CHAPTER VII

VAPOUR-PRESSURES OF SOLUTIONS

1. **Historical.**—The fact has been known for a long time that water which holds non-volatile matter in solution boils at a higher temperature than pure water. Experiments were made many years ago to measure the influence of the dissolved substance on the boiling-point of water; Faraday[1] in 1822, and Griffiths[2] in 1824, made determinations with a number of salts. Some years later Legrand[3] carried out a great many similar measurements, but without arriving at any general law.

This method of attacking the problem, it is true, is the first to suggest itself, but nevertheless it is not the most rational. To determine the boiling-point is to determine the temperature whereat the vapour-pressure of the solution is equal to that of the atmosphere; the influence of the dissolved substance is therefore measured by the increase of temperature which is needed to counterbalance exactly the decrease of vapour-pressure. Now, as the exact connexion between the changes of vapour-pressure and the changes of temperature is unknown, it follows that the explanation of the results obtained by experiments such as those referred to is attended with difficulties.

The problem was reversed by Gay-Lussac and Prinsep; these investigators measured the pressures at equal temperatures, instead of the temperatures at equal pressures. Gay-Lussac found the vapour-pressure of a solution of

[1] *Ann. Chim. Phys.* (2) **20**, p. 324. [2] *Journal of Science*, **78**, p. 90.
[3] *Ann. Chim. Phys.* (2) **59**, p. 423 [1835].

common salt, of spec. gravity 1·096, to be $\frac{9}{10}$ that of pure water, and Prinsep asserted that this relation was maintained at all temperatures.

The whole subject of the decrease of vapour-pressures caused by solution of salts was taken up by von Babo. The original memoirs are not accessible to me; I gather from the abstracts [1] that he expressed the relation between the quantity of salt in solution and the excess of the vapour-pressure of water over that of the salt-solution by two geometrical series. From experiments with calcium chloride, and subsequently with many other salts, he concluded that the relation is the same at all temperatures.

2. **Work of Wüllner.**—The investigations of Wüllner [2] concerning the vapour-pressures of solutions, and especially salt-solutions, began in 1856. The apparatus consisted of several glass-tubes, closed above and connected with one another by canals in an iron plate. Each tube contained mercury and a few cubic centimetres of the salt-solution to be examined; one tube contained mercury and pure water. The whole apparatus was immersed in a bath which was maintained at a constant temperature. When the pressures were sufficiently diminished, the differences between the pressures of the salt-solutions and the pressure of the pure water could be directly determined by reading the levels of the columns of mercury. The general result arrived at by Wüllner may be expressed by saying that *the diminution of the vapour-pressure of water caused by substances dissolved therein, which substances do not themselves exert any noticeable pressure at the temperature of the experiment, is proportional to the quantity of substance in solution.* It does not matter whether the substance be a single salt or a mixture of salts.

Wüllner was able to confirm the statement of Prinsep, that the ratio of the vapour-pressures of water and solu-

[1] *Jahresberichte*, 1848–1849, p. 93; 1857, p. 72.

[2] *Dissertation*, 1856. *Pogg.* **103**, p. 529 [1858]; **105**, p. 85; **110**, p. 564 [1858–60].

tions is independent of the temperature only in special cases —e.g. for sodium chloride and Glauber's salt, and, somewhat strangely, for several mixtures of salts, the constituents of which mixtures, Wüllner said, did not themselves exhibit the simple relation in question. A dependence of the ratio upon temperature was established in the cases of many salts; sometimes the ratio increased, and sometimes it decreased, as the temperature rose. Putting v as the decrease of the vapour-pressure caused by solution of 1 part of a salt in 100 parts of water, and P as the vapour-pressure of pure water, then the ratio $\frac{P}{v}$ was found by Wüllner to be constant for sodium chloride and Glauber's salt, but not to be constant for other salts. Wüllner represented the relation, empirically, as a function of the pressure P; he gave the following formulæ:—

NaCl	$V = \cdot00601\ P$
Na_2SO_4	$= \cdot00236\ P$
$NaNO_3$	$= \cdot00315\ P + \cdot000000907\ P^2$
KCl	$= \cdot00390\ P + \cdot000000538\ P^2$
K_2SO_4	$= \cdot00383\ P - \cdot0000019\ P^2$
KNO_3	$= \cdot00196\ P + \cdot00000108\ P^2$
$KOH.2H_2O$	$= \cdot003320\ P - \cdot00000432\ P^2$ to 53°
	$= \cdot002863\ P$ from 53° to 100°
$NaOH.2H_2O$	$= \cdot004089\ P$
$CaCl_2.6H_2O$	$= \cdot002474\ P - \cdot000000522\ P^2$

In the cases of potash, soda, and calcium chloride it was necessary for Wüllner to regard the quantities of water expressed in the formulæ given above as in chemical combination with the compounds in order to bring the results within the law of proportional increase of vapour-pressure. Other compounds which generally crystallise with water of crystallisation—e.g. Na_2SO_4, $NiSO_4$, $Ca(NO_3)_2$, and Na_2HPO_4—behaved as anhydrous salts. Most of the deviations from the simple law which Wüllner noticed may perhaps be attributed to errors in his measurements, so that the law cannot be regarded as finally and conclusively established.

No definite connexion was traced by Wüllner between the diminutions of the vapour-pressures of the solutions and the other properties of the salts examined; this might be foreseen from the observation, already noticed, that the vapour-pressures were influenced by changes of temperature in a very irregular way. Nevertheless, if the diminutions of vapour-pressure are referred to quantities related to one another in the proportion of the molecular weights of the dissolved compounds, and not to equal quantities, as was done by Wüllner, one cannot fail to notice an approximate constancy in these 'molecular' diminutions of vapour-pressure.[1] I have calculated these diminutions, approximately, for the vapour-pressures at 100°. Solutions containing one molecular weight, in grams, of the following salts, in 1,000 grams of water, showed the diminutions of vapour-pressures which are noted: $NaCl = 27$, $Na_2SO_4 = 26$, $NaNO_3 = 25$, $KCl = 24$, $K_2SO_4 = 32$, $KNO_3 = 22$, $KOH.2H_2O = 19$, $NaOH.2H_2O = 22$, $CaCl_2.6H_2O = 35$. These numbers show a rough approximation. Some of the values—for instance, the small number for potash—may perhaps be ascribed to inaccuracies in the estimations of the percentage contents of the solutions.

I append a few examples, taken from the very large collection of experimental data, in order to illustrate the relations which have been sketched.

Sodium Chloride

Temp.	p	5 p. ct.	10 p. ct.	20 p. ct.	30 p. ct.	Mean. 1 p. ct.	$\frac{v}{p}$
19·9°	17·38	0·98	1·47	—	4·06	·149	·0086
35·0	41·82	1·79	3·11	—	8·13	·30	·0072
49·8	91·09	2·84	5·81	11·36	18·20	·62	·0068
64·8	185·27	—	9·88	21·45	—	1·09	·0059
82·2	388·33	—	21·58	46·20	—	2·24	·0058
100·5	775·40	—	44·90	92·41	—	4·45	·0057

[1] This inference was drawn by me in 1883, when I was preparing the first edition of my *Lehrbuch*, part i. of which appeared in January 1884. The same conclusion was established, with certain necessary limitations,

Potassium Nitrate

Temp.	P	5 p. ct.	10 p. ct.	20 p. ct.	25 p. ct.	Mean. 1 p. ct.	$\frac{V}{P}$
38·4°	50·38	·49	·99	1·88	2·38	·099	·00196
660	155·13	1·88	3·56	6·52	8·31	·33	·00213
100	369·28	4·43	7·88	16·00	19·60	·81	·00220
1980	776·48	11·29	21·21	40·46	—	2·15	·00277

Calcium Chloride

Temp.	P	15·8 p. ct.	34·4 p. ct.	83·5 p. ct.	Mean. 1 p. ct.	$\frac{V}{P}$
16·20°	13·71	·50	·97	2·80	·032	·00233
40·66	56·71	2·68	4·96	11·56	·144	·00254
60·00	148·79	5·28	11·25	26·70	·340	·00228
80·60	363·43	11·94	27·01	68·18	·806	·00222
99·30	741·28	23·00	53·95	133·51	1·582	·00214

If the mean values, given in the last column but one, are multiplied by the numbers expressing percentages placed at the heads of some of the other columns, the results agree to a few millimetres with the observed numbers, and so confirm the law of proportionality within these limits. But as the diminutions of vapour-pressure are themselves rather small, the accuracy of this confirmation of the law is not very great.

Wüllner found extremely complicated relations in the examination of solutions which contained several salts simultaneously. The diminution of vapour-pressure was frequently equal to the sum of the diminutions caused by the single salts; in other cases it was different from this sum. No relation could be discovered between the change of the ratio $\frac{V}{P}$ with change of temperature for mixtures and for their constituent salts; the only regularity which could be traced was that of the proportion between the decrease of vapour-pressure and the total quantity of

very soon afterwards by the work (to be noted immediately) of Tammann, Raoult, and others. I have reprinted the text, as above, from the first edition, without change.

substance in solution. Here also it may be asked how much of the observed deviation ought to be ascribed to errors of experiment.

3. **More recent investigations.**—In the year 1879 Pauchon[1] threw doubt on the relation between the vapour-pressures and the contents of salt-solutions which had been put forward by Wüllner. Pauchon represented the decrease of vapour-pressure calculated for a 1 per cent. solution, d, as a function of the vapour-pressure of pure water, ϕ, by an expression having the form $d = a\phi + b\phi^2$. This expression held good to 35°. The two constants a and b were dependent on the concentration. For KCl, NaCl, KNO_3, and K_2SO_4, a increased, and for Na_2SO_4 it decreased, as temperature increased.

A few years later Tammann published an extended investigation into the subject of the vapour-pressures of salt-solutions; this investigation led him to a conclusion similar to that stated on p. 159, viz. that the molecular diminutions of vapour-pressures caused by similar salts have nearly equal values. Tammann's experimental method was simpler and more appropriate than the older method. The solution was placed in one limb of a U tube which was nearly filled with mercury; the air was removed by boiling the liquid, and this limb was closed by the blowpipe. The other limb was connected with a manometer and an air-pump, and the U tube was immersed in a bath maintained at a convenient temperature. The vapour-pressure of the solution was found by reading the level of the mercury in both limbs and the manometer, after the pressure had been adjusted to a convenient amount. The vapour-pressure of water was determined by simultaneous observations made with a U tube properly arranged with pure water in place of the salt-solution.

A comparison of the observations made at different concentrations confirmed the statement of Pauchon that Wüllner's law of proportionality is not strictly accurate.

[1] *Compt. rend.* 89, p. 752.

The sulphates of sodium, ammonium, and magnesium (the last with $6H_2O$), $BaCl_2.2H_2O$, and ammonium bromide agreed with the law within the limits of experimental error; but the relative diminutions of vapour-pressure were found to increase for most salts as the concentrations increased; the vapour-pressures, however, decreased for nitrate of sodium and potassium and chlorate of potassium; in some cases an increase of vapour-pressure was succeeded by a decrease, as concentration increased.

If the molecular diminution of vapour-pressure, determined for the most dilute solution of each salt, is put as $s = \frac{p - p_1}{p.m}$ M, where p = the vapour-pressure of water, p_1 = the vapour-pressure of the solution, m = the percentage composition of the solution, and M = the molecular weight of the salt, the following table is obtained:—

	s		s
KCl	·330	NH_4Br	·302
KBr	·322	$FeSO_4.5H_2O$	·147
KI	·312	$CuSO_4.5H_2O$	·132
KF	·343	$NiSO_4.6H_2O$	·132
KSCN	·327	$CoSO_4.6H_2O$	·121
K_2SO_4	·347	$ZnSO_4.6H_2O$	·122
KNO_3	·302	$MnSO_4.6H_2O$	·109
$KClO_3$	·260(?)	$MgSO_4.6H_2O$	·143
$K_2CO_3.1\frac{1}{2}H_2O$	·391	$BeSO_4.4H_2O$	·141
K_2CrO_4	·409	$Al_2(SO_4)_3.18H_2O$	·209
RbCl	·321	NaCl	·344
CsCl	·345	NaBr	·359
NH_4Cl	·273	NaI	·333
$Li_2SO_4.H_2O$	·348	Na_2SO_4	·337
$BaCl_2.2H_2O$	·467	$NaNO_3$	·302
$SrCl_2.6H_2O$	·406	$NaClO_3$	·307
$CaCl_2.6H_2O$	·422	Na_2CO_3	·389
$MgCl_2.6H_2O$	·460	$Na_2S_2O_3$	·384
$BaBr_2.2H_2O$	·505	$LiCl.2H_2O$	·359
$SrBr_2.6H_2O$	·450	$LiBr.2H_2O$	·367
$CaBr_2.6H_2O$	·513	$LiI.3H_2O$	·347
$MgBr_2.6H_2O$	·504	$LiNO_3.3H_2O$	·377

The numbers are not perfectly comparable, as they were determined for concentrations differing somewhat from one another; nevertheless they show that chemically similar

salts certainly produce nearly equal molecular diminutions of vapour-pressure.

4. **Investigations of Emden.**—While all previous observers were fairly agreed in saying that the ratio between the vapour-pressure of a solution and that of pure water varies with temperature, they differed as to the direction of this variation. Wüllner found that the proportional lowering of vapour-pressure produced by sodium chloride was constant at all temperatures; Tammann found a decrease, and Pauchon an increase, in the proportion consequent on raising the temperature.

Emden [1] turned his attention especially to this part of the subject. To ensure accurate measurements Emden used an experimental arrangement, proposed by Konowaloff,[2] consisting essentially of a three-limbed tube, fitted with stop-cocks, which allowed of the easy and complete expulsion of air from the liquid under examination. Different solutions of sodium, potassium, and calcium chlorides, sodium and potassium nitrates, and potassium copper and zinc sulphates were employed. Especial pains were devoted to the difficult task of avoiding the constant errors. To determine whether the law of von Babo, which asserts that the vapour-pressures of water and solutions are always in the same proportion, was valid or not, interpolation-formulæ were employed of the form suggested by Magnus, $p = a\,10^{\frac{bt}{c+t}}$. If this equation holds good for water, and a similar equation, $p' = a'\,10^{\frac{b't}{c'+t}}$, holds for the salt-solution, and if the ratio $p : p'$ is independent of the temperature, then the temperature-function must disappear from the quotient $\frac{a\,10^{\frac{bt}{c+t}}}{a'\,10^{\frac{b't}{c'+t}}}$ that is, b must $= b'$ and $c = c'$; hence it follows that $p : p' = a : a'$.

The calculations were made by finding whether the ob-

[1] *Wied. Ann.* **31**, p. 145 [1887] [2] *Ibid.* 4, p. 34 [1881].

served numbers were in keeping with an expression of the form, $p' = a' 10^{\frac{a t}{b+t}}$, where a and b were the constants of the formula for water, viz. $a = 7{\cdot}47737$ and $b = 236{\cdot}57$. This formula was found to apply within the limits of the experimental errors. Hence there is nothing against the statement that *the law of von Babo is valid within the temperature-interval* 20° *to* 95°.

An examination of Wüllner's statement showed, as former examinations had shown, that this statement is only approximately accurate, and that the values obtained for p show deviations in both directions from the calculated values, depending on the nature of the salt examined.

5. **Vapour-pressures at low temperatures.**—The method made use of in the investigations which have been described consisted essentially in measuring the vapour-pressure of the liquid under examination by means of a column of mercury. While this process gives very satisfactory results at high temperatures, it is almost quite inapplicable at low temperatures; for the vapour-pressure of water is equal to only ·4 centim. of a column of mercury at 0°, and to 1·74 centims. at 20°. The decrease which is caused in the vapour-pressure of water by solution of a salt seldom amounts to more than one-tenth of the value of the pressure of the water; this would amount only to ·04 centim. at 0°, which is nearly as small a quantity as can be determined by measuring the height of a column of mercury. But measurements of the vapour-pressures of solutions of salts at low temperatures are of especial interest, because these values are often used as the foundations of theoretical discussions.

Moser[1] conducted experiments with the object of determining these values. He partly filled one U tube with water, and another with a salt-solution; each limb of both tubes was furnished with stopcocks, and they could be brought into communication with one another. When the air had been removed, the apparatus was kept for a long

[1] *Wied. Ann.* **14**, p. 72 [1881].

time at a constant temperature, one limb of the water-tube being in communication with one limb of the tube which contained the salt-solution; the differences of the levels of the liquids in the two tubes gave the lowering of the vapour-pressure, the specific gravity of the salt-solution being taken into consideration. As the differences of pressure were read off in terms of a column of water, the errors of reading exerted an influence on the result thirteen times less than when mercury was used.

The results obtained by Moser agreed with those of Wüllner.

A similar arrangement, which seems to have advantages over that just mentioned, was described by G. J. W. Bremer.[1] This consisted of several (e.g. four) small flasks, with a tube bent into the form of a syphon ground into the neck of each. The longer under limbs of the syphon-formed tubes were connected by a cross-piece, which carried an additional wider tube, connected in its turn with a large pipette by means of a piece of thick-walled caoutchouc tubing. Water was poured into one of the flasks, and the salt-solutions into the others; the syphon-formed tubes were set in their places and were made tight by pouring mercury around the parts which fitted into the necks of the flasks; the large pipette was partly filled with olive-oil, and the air was then pumped out of the whole apparatus through the open end of the pipette. After the temperature had been made equal, the difference between the vapour-pressures of the solutions and that of pure water was determined by properly adjusting the pipette, and reading the levels of the columns of oil in the longer limbs of the syphon-formed tubes. As the liquid used as a manometer-fluid was olive-oil of spec. gravity ·9276 $(1 - \cdot 000708\, t)$ the readings were about fifteen times more accurate than those of a mercury-column. Several experiments with solution of calcium chloride agreed well among themselves.

Quite a different process, applicable at low temperatures, was put forward by von Helmholtz.[2] If the air in a speci-

[1] *Rec. trav. Pays-Bas*, 6, p. 122 [1887]. [2] *Wied. Ann.* 27, p. 568 [1886].

fied space is suddenly rarefied, this adiabatic process results in a decrease of temperature which can be calculated by a well-known thermodynamical formula. If the air is saturated with water-vapour, the lowering of temperature, corresponding with the smaller expansion, suffices to produce a cloudiness. If the air is in contact with a salt solution, it is not saturated as regards water, and a decrease of pressure of corresponding amount is required to bring about such a fall of temperature as shall cause saturation, and therefore the formation of a cloud. Reference must be made to the original memoir for details, and for the method of calculation. Experiments were conducted with solutions of sulphuric acid and common salt; the first gave results which agreed well with those obtained by Regnault; the results for common salt differed from those of Wüllner.

Finally, J. Walker [1] has made determinations of the vapour-pressures of salt-solutions at low temperatures by a method proposed by me. The method consists in slowly passing a stream of air through a system of three Liebig's bulbs, and a U tube containing pumice soaked in sulphuric acid. The first and second bulbs contain the solution which is being examined, and the third contains pure water. As the air streams through the first and second bulbs it takes up a quantity of water corresponding with the vapour-pressure, by far the greater part of this being taken from the first bulb, the solution in the second bulb indeed undergoing no notable change. In passing through the third bulb, which contains water, the air takes up water-vapour sufficient to saturate it; and finally the whole of the water which the air contains is given up as it passes over the pumice moistened with sulphuric acid. The loss of weight of the bulb containing water, and the gain of weight of the absorption-tube, are determined after the experiment has continued for a long time, generally for twenty-four hours. The proportion of these two gives immediately the relative lowering of the vapour-pressure of the salt-solution; for as

[1] *Zeitschr. f. physikal. Chemie*, **2**, p. 602 [1888].

much water is taken up by the air from the water-bulb as corresponds with the difference of the vapour-pressures over the solution and over pure water, while the total water given up to the sulphuric acid is a measure of the vapour-pressure of pure water. The method rests on the suppositions that the vapour-pressures of water and the salt-solution are the same in air as *in vacuo*, and that water-vapour obeys the law of Boyle: the investigations of Regnault have shown both suppositions to be permissible.

The results obtained by this method are given in the table which follows. The parts of the dissolved substance per 100 parts of water are given under g; c gives the molecular lowerings of vapour-pressure, i.e. the relative lowering of vapour-pressure brought about by one molecule of the substance dissolved in 100 molecules of water. The values of c are obtained by the formula $c = \frac{a}{s} \cdot \frac{m}{18 \times g}$, where a = loss of weight of the bulb which contained water, s = gain of weight of the sulphuric acid tube, m = molecular weight of the dissolved substance, 18 = molecular weight of water, and g = percentage contents of the solution.

	g	c	c (Emden)
NaCl	5·96	2·07	2·12
„	18·60	2·18	2·14
„	32·265	2·29	2·25
KCl	7·66	2·02	1·81
NH_4Cl	5·697	1·99	2·08
$NaNO_3$	8·791	1·97	—
KNO_3	11·222	1·61	1·66
$CaCl_2$	11·386	3·30	3·39
$SrCl_2$	16·002	3·28	—
$BaCl_2$	21·443	3·00	—
$MgCl_2$	4·791	3·57	—
„	9·691	4·01	—
$ZnCl_2$	8·624	3·45	—
$ZnSO_4$	17·889	1·26	1·44
$CuSO_4$	16·061	1·43	1·26
$CO(NH_2)_2$	6·667	1·11	—
„	13·333	1·07	—
„	26·667	0·91	—
$C_{12}H_{22}O_{11}$	38·000	1·30	—
$H_2C_2O_4$	5·000	1·58	—

The last column contains the values of c calculated from Emden's results: the two series of values for c agree fairly well. The observations made with solutions of common salt of different concentrations bring out the fact, which had been noticed repeatedly, that more concentrated solutions of this salt exhibit relatively greater lowerings of vapour-pressure than more dilute solutions.

Other methods might be proposed, besides those noticed, for determining the vapour-pressures of salt-solutions at low temperatures; especially might the use of a sensitive hygrometer be suggested. But no investigations in such directions have been made known as yet.

6. **Investigations of Raoult.**—The attempts made to advance our knowledge of the laws which express the vapour-pressures of dilute solutions were greatly hindered by the circumstance that water was the only solvent used by the older investigators, and that compounds belonging to the class of salts alone were examined. But it is just in the cases of salts, and almost in these cases only, that deviations occur from the simple laws which were soon arrived at when the investigation was extended to other substances and other solvents.

The first investigations of this kind were conducted by Raoult.[1] He used ether as the solvent, and employed the barometric method for measuring the vapour-pressures. The following general results were obtained.

Influence of temperature.—The ratio $\frac{p-p'}{p}$ has the same value between 0° and 20°; p = vapour-pressure of pure ether, p' = vapour-pressure of an ethereal solution. The relative lowering of vapour-pressure, $\frac{p-p'}{p}$, is therefore independent of temperature.

Influence of concentration.—For solutions of medium concentration the relative lowering of vapour-pressure, $\frac{p-p'}{p}$, is proportional to concentration. If g = the weight

[1] *Compt. rend.* **103**, p. 1125 [1886].

of dissolved substance in 100 parts of ether, and m = the molecular weight of the dissolved substance, the expression $c = \frac{p - p'}{p} \cdot \frac{m}{g}$ gives the molecular lowering of vapour-pressure.

Influence of the nature of the dissolved substance.—The molecular lowering of vapour-pressure is independent of the nature of the dissolved substance. The following table exhibits the validity of this law.

		m	c
Carbon hexachloride	C_2Cl_6	237	·71
Turpentine	$C_{10}H_{16}$	136	·71
Methyl salicylate	$C_6H_8O_3$	152	·71
Methyl azocuminate	$C_{22}H_{26}N_2O_4$	382	·68
Cyanic acid	$CNOH$	43	·70
Benzoic ,,	$C_7H_6O_2$	122	·71
Trichloracetic acid	$C_2Cl_3HO_2$	163·5	·71
Benzaldehyde	C_7H_6O	106	·72
Caprylic alcohol	$C_8H_{18}O$	130	·73
Cyanamide	CN_2H_2	42	·74
Aniline	C_6H_7N	43	·71
Mercuric ethide	$C_4H_{10}Hg$	258	·69
Antimony chloride	$SbCl_3$	228·5	·67

Although the nature of the substances in solution varies much, yet the molecular lowerings of vapour-pressure show only very small differences.

The first of the foregoing statements made by Raoult is identical with the statement of von Babo (p. 157), and the second is identical with that of Wüllner (p. 157). Raoult's third statement agrees with that put forward by me (p. 159) so far that the nature of the dissolved substance seems to be without influence when ether is the solvent, but when aqueous solutions of salts are examined different molecular lowerings of vapour-pressure are observed, and these are dependent on the type to which the salt belongs.

At a somewhat later time, Raoult[1] was led to another law which had not been observed before. This law expresses the relative lowerings of vapour-pressures observed

[1] *Compt. rend.* **104**, p. 1430 [1887].

in different solvents. *The lowerings of vapour-pressures of solutions in different solvents are equal when the proportion of the number of molecules of the dissolved substance to the number of molecules of the solvent is the same.*

Twelve solvents were chosen, and many different substances were dissolved in these. If the relative lowerings of vapour-pressures are calculated for one molecule of each substance in 100 molecules of the solvent, the following numbers are obtained:—

	Molecular weight	Molecular lowering of vapour-pressure 1:100
Water	18	·0102
Phosphorus trichloride	137·5	·0108
Carbon disulphide	76	·0105
Carbon tetrachloride	154	·0105
Chloroform	119·5	·0109
Amylene	70	·0106
Benzene	78	·0106
Methyl iodide	142	·0105
Methyl bromide	109	·0109
Ether	74	·0096
Acetone	58	·0101
Methyl alcohol	32	·0103

If n = the number of molecules of the dissolved substance, and N = the number of molecules of the solvent, then

$$\frac{p - p'}{p} = c\frac{n}{N},$$

where c is a constant the value of which falls between ·96 and 1·09.

7. **Other methods of formulation.**—The deviations from proportionality between the relative lowering of vapour-pressure and the quantity of substance dissolved in 100 parts of the solvent, which had led Raoult to confine the statement of his law to medium concentrations, induced him to adopt a more complicated formula,[1] which he afterwards abandoned in favour of another method of calculation[2] adapted to the special experiments. The

[1] *Compt. rend.* **104**, p. 976 [1887].
[2] *Zeitschr. f. physikal. Chemie*, **2**, p. 353 [1888].

following consideration will show that the foregoing formula is only applicable to solutions of small concentration. If we put $c = 1$, the equation takes the form

$$\frac{p - p'}{p} = \frac{n}{\text{N}}.$$

If $n = \text{N}$, i.e. if the number of the molecules of solvent and dissolved substance is the same, then

$$\frac{p - p'}{p} = 1,$$

and hence p' must $= 0$. That is, the vapour-pressure of a solution containing an equal number of molecules of solvent and dissolved substance must be *nil*; but this is against the experimental facts.

The actual relations are said by Raoult to be expressed very accurately by slightly changing the form of the equation :—

$$\frac{p - p'}{p} = c\frac{n}{\text{N} + n}.$$

This expression does not assert the relative lowering of vapour-pressure to be proportional to the ratio of the number of molecules of the dissolved substance and the solvent, but it says that *the relative lowering of vapour-pressure is proportional to the ratio of the number of molecules of the dissolved substance to the total number of molecules in the solution.* The factor of proportionality is nearly equal to unity.

It is easy to see that this formula does not lead to conclusions which are contradictory to the facts. If n increases, the fraction $\frac{n}{\text{N} + n}$ always remains less than one, and p' therefore always retains a finite value. It is only when n is infinitely large compared with N, i.e. when no solvent is present, that p' becomes equal to zero.

The following measurements made by Raoult[1] (taken

[1] *Zeitschr. f. physikal. Chemie*, **2**, p. 353 [1888].

from his memoir of 1888) show that the formula leads to results which are in agreement with those observed with more concentrated solutions :—

Turpentine in Ether

$\frac{n}{N+n}$	$100\,\frac{p-p'}{p}$	
	Observed	Calculated
5·9	6·0	5·3
12·1	11·9	10·9
23·4	21·9	21·1
35·5	32·4	32·0
47·9	43·8	43·1
64·5	57·9	58·0

The numbers under 'Calculated' are obtained by assuming that $c = \cdot 90$.

Nitrobenzene in Ether ; $c = \cdot 74$

$\frac{n}{N+n}$	$100\,\frac{p-p'}{p}$	
	Observed	Calculated
6·0	5·5	4·4
17·9	14·2	13·2
35·5	25·6	26·3
53·2	38·0	39·4
75·9	55·6	56·2
84·0	64·5	62·2

Aniline in Ether ; $c = \cdot 90$

$\frac{n}{N+n}$	$100\,\frac{p-p'}{p}$	
	Observed	Calculated
3·85	4·0	3·4
7·7	8·1	6·9
14·8	15·4	13·3
20·5	19·7	18·4
49·6	42·4	44·6
68·7	59·6	61·8

ETHYL BENZOATE IN ETHER; $c = \cdot 90$

$\frac{n}{N+n}$	$100\,\frac{p-p'}{p}$	
	Observed	Calculated
4·9	5·1	4·4
9·6	9·1	8·6
27·1	24·8	24·4
53·0	47·1	47·7
75·5	70·0	67·9
94·4	87·6	85·0

These numbers show that the formula represents the results even to very great concentrations (the last solution of ethyl benzoate contained less than 3 per cent. ether to 97 per cent. of the dissolved substance); but the fact must not be overlooked that the dilute solutions always gave larger values than those calculated by the formula. The value of the constant, c, which is generally about ·9, approaches unity for those solutions which are of medium concentration. If the numbers given on p. 169, which refer to one molecule of the dissolved substance in 100 parts by weight of ether, are calculated to 100 molecules of the solution, the numbers obtained clearly approach the value ·01; the same result holds good for the numbers in the table on p. 170. The factor, c, may, then, be taken as 1 for dilute solutions; the formula becomes,

$$\frac{p - p'}{p} = \frac{n}{N + n}.$$

The decrease of vapour-pressure produced by the dissolved substance is related to the vapour-pressure of the solvent as the number of molecules of the dissolved substance is related to the total number of molecules.

8. **Applications.**—It follows from the foregoing statement that the measurement of the lowering of vapour-pressure can be used as an aid in finding the molecular weight of a substance. If the molecular weight of the substance in

solution, m, is unknown, the number of molecules in solution may be put as $\frac{s}{m}$, where s = weight of substance dissolved in one molecular weight of the solvent (all weights being expressed in grams). Then putting $n = \frac{s}{m}$, and $\text{N} = 1$, in the equation $\frac{p - p'}{p} = \frac{n}{\text{N} + n}$, and solving this equation for m, it follows that $m = \frac{s\,p'}{p - p'}$. For instance, Raoult examined a solution of 11·346 grams turpentine in 100 grams ether; he found $p' = 36{\cdot}01$ centims. and $p = 38{\cdot}3$ centims. As the molecular weight of ether is 74, the value of s was $\frac{11{\cdot}346}{100}74 = 8{\cdot}396$; hence $m = \frac{8{\cdot}396 \times 36{\cdot}01}{2{\cdot}29} = 132$. As the actual molecular weight of turpentine-oil is 138, the value found by this method is sufficiently near the true value.

This method makes it possible to find the molecular weight of any substance which dissolves in a volatile solvent. As before the introduction of this method, only the molecular weights of those substances which were gasifiable without change could be determined, the sphere within which determinations of molecular weights can be made has been very much extended. It becomes, then, a matter of much importance to find a certain and accurate process for measuring the vapour-pressures of solutions.

Raoult made almost exclusive use of the immediate method of determining vapour-pressure by placing the solution over mercury in the barometric vacuum. I do not give the details of procedure which Raoult[1] lays down as giving satisfactory results. All the 'statical' methods of measuring vapour-pressure, i.e. the methods which consist in determining the pressure of the vapour given off by a solution, labour under two disadvantages. One is, that the portion of the solvent which becomes vapour is proportion-

[1] *Zeitschr. f. physikal. Chemie*, **2**, p. 353 [1888].

ately very small; should any more volatile impurity be present, e.g. an absorbed gas, this passes into the vapour and increases the pressure to a disproportionate extent. The second disadvantage is that the equilibrium between the vapour and the solution is dependent on the nature of the solution only in so far as this is in contact with the vapour. If the solvent should evaporate superficially at the beginning of the experiment, a more concentrated layer will be formed, and the vapour-pressure will be too small. On the other hand, if any of the vapour should be condensed by some diminution of the space, a superficial layer of the pure solvent will be formed, and the vapour-pressure will be too large. G. Tammann has very carefully studied and clearly indicated the influence of both these conditions on measurements of vapour-pressures.[1]

E. Beckmann [2] has also fully examined the difficulties of the statical method, in his attempts to develop a methodical process for determining molecular weights on the basis of measurements of vapour-pressures. The difficulties caused Beckmann to abandon this method. A method which was partially statical alone gave fairly good results; the error due to the presence of air was diminished by making the space containing the vapour large, and the changes of concentration at the surface of the solution were rendered harmless by agitating the liquid. The pressure of the vapour was not measured directly, but was obtained from the weight of liquid which evaporated. The small flask *E* (fig. 22) was filled with ether and weighed accurately. It was then connected with the flask *A* by means of the tube *B*, which was ground into the neck of *E*. Before the experiment began a partial vacuum was produced in *A*; this vacuum was measured by the manometer *C*. It was not necessary to remove the whole of the air from *A*, but only to produce a partial vacuum by the use of a good water-air pump; but care had to be taken that the remaining

[1] *Wied. Ann.* **32**, p. 683 [1887].
[2] *Zeitschr. f. physikal. Chemie*, **4**, p. 532 [1889].

air should have exactly the same pressure in each experiment. On opening the stopcock *B*, a quantity of ether, *a*, was evaporated; this depended on the temperature of *E* and *A*, and was measured by re-weighing *E*. A second experiment was then made with a solution, care being taken that the temperature of *E* did not vary more than ·01° from what it was in the first experiment, and a smaller loss of

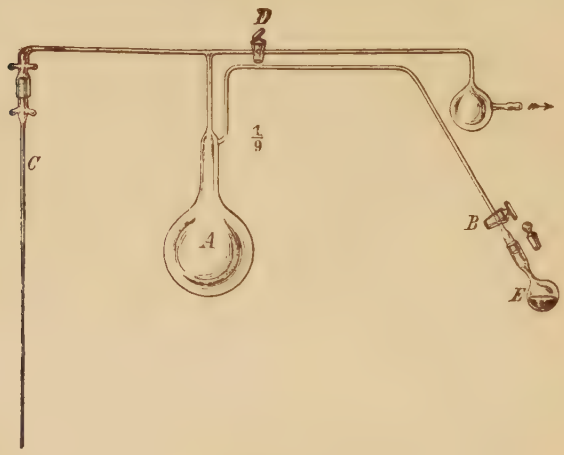


Fig. 22

weight, a', was found. Now as the quantities a and a' are proportional to the pressures p and p', under the conditions observed, a and a' may be substituted in the equation given on p. 174, and we have $m = \dfrac{s\,a'}{a - a'}$. Some measurements gave the following values :—

	a	a'	s	m found	m calculated
Camphor . .	1·5754	1·5086	7·35	157	152
Aniline . . .	1·5754	1·4785	6·04	87	93
Ethyl benzoate .	1·5754	1·4829	9·26	141	150

The observed molecular weights are sufficiently near the calculated values.

The process given by me, and described for aqueous solutions on p. 166, exemplifies the change to the dynamical methods. As the process is frequently required for finding the molecular weights of organic compounds, and as aqueous solutions of these compounds are rarely obtainable, Will and Bredig[1] have worked out a process for alcoholic solutions which differs from that described on p. 166 chiefly in that the quantity of solvent evaporated is not determined by absorption, but from the loss of weight of the apparatus. Dry air is led, by an aspirator, through a bulb-apparatus containing the solution, and then through a similar apparatus containing pure alcohol. The loss of weight in the first apparatus, b_1, corresponds with the vapour-pressure p', and the loss of weight in the second apparatus, b_2, corresponds with the vapour-pressure $p - p'$. The formula for calculating the molecular weight is then

$$m = \frac{s\, b_1}{b_2}.$$

To insure the complete saturation of the air with alcohol-vapour, each bulb-apparatus was furnished with 9 bulbs; both were placed in large water-baths, the temperatures of which were kept equal. The current of air was maintained for 24 hours, at the rate of about 1 litre per hour. Some of the results are given in the following table:—

	b_1	b_2	s	m found	m calculated
Nitrobenzene . .	2·034	·0684	4·1	122	123
Acetamide . .	·6073	·0525	5·04	58	59
Benzoic acid . .	1·8315	·0731	4·28	107	122
Atropine . . .	1·467	·027	5·05	275	289
Vanilline . . .	1·6895	·0312	2·4	130	152

This method is thus shown to be applicable for laboratory-purposes.

[1] *Berichte*, **22**, p. 1084 [1889].

9. **Beckmann's boiling-method.**—In place of determining the vapour-pressures of solutions at equal temperatures, it is evidently possible to find the temperatures at which the vapour-pressures are equal. If the general form of the curve of vapour-pressure of the solvent is known, it is easy to calculate the vapour-pressure of the solvent which corresponds with the higher boiling-point of the solution, and thus to obtain the data needed for calculating the molecular weight of the dissolved substance.

The calculation is sufficiently simple. Let the curve of vapour-pressure of the solvent be $d\,d$ (fig. 23), the temperatures being taken as abscissæ and the pressures as ordinates. The part of the curve which corresponds with the observed small difference of temperature may be taken as a straight line; then putting t_1 = boiling-point of the solvent, t_2 = boiling-point of the solution, $p' = b$ = atmospheric pressure, p becomes $b + \beta(t_2 - t_1)$, where β = the tangent of the angle which the curve of vapour-pressure forms with the axis of abscissæ at the place under consideration, i.e. at mean atmospheric pressure.

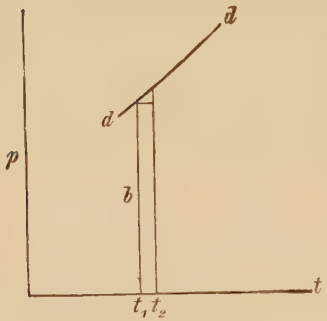


FIG. 23

There are several ways of finding β. If the curve of vapour-pressure of the solvent has been determined by separate experiments, the value of $\beta = \frac{d\,p}{d\,t}$ can be obtained by an interpolation-formula or by a graphical method. Or measurements may be made of the corresponding boiling-points at the greatest possible differences of barometric pressure—which must be measured accurately—and the value of β may then be found by the equation $\beta = \frac{b' - b''}{t' - t''}$, where b' and b'' are the barometric readings

and t' and t'' are the boiling-points. Arrhenius[1] has shown that use may also be made of the formula of the dynamical theory of heat $\frac{dp}{dt} = \frac{\rho}{v\,\mathrm{T}}$, where ρ = heat of vaporisation, v = volume occupied by the saturated vapour, and T = the absolute boiling-temperature. Replacing v by its value from the gas-equation $p\,v = \mathrm{R\,T}$, the formula obtained is $\frac{dp}{dt} = \frac{\rho\,p}{\mathrm{R\,T^2}}$. Now if molecular quantities are considered, R = 2 cals.; and in this case ρ must be taken as the molecular heat of vaporisation. Hence

$$\beta = \frac{\rho\,p}{2\,\mathrm{T}^2};$$

by this formula β is found from measurements of the heat of vaporisation, the pressure, and the absolute boiling-temperature. This formula can give altogether correct results only when the supposition on which it depends is fulfilled, viz. that the equation for gases $p\,v = \mathrm{R\,T}$ is applicable to the vapour under examination. The specific gravity of the vapour is generally greater than that which the formula leads to, and therefore corresponding deviations occur.

The first formula $\frac{dp}{dt} = \frac{\rho}{v\,\mathrm{T}}$ does not imply the validity of the equation for gases; but it is very difficult to obtain accurate values for the volume, v, of the saturated vapour.

The greatest difficulty in the procedure lies in the estimations of temperature. The differences of temperature are very small; this difficulty may be got over by using very delicate thermometers. But the temperature of the boiling-liquid must be determined, not that of the vapour; and it has been recognised since Rudberg's researches that the temperature of a liquid boiling under ordinary conditions varies considerably. This variability depends on the production of bubbles of vapour within the

[1] *Zeitschr. f. physikal. Chemie*, 4, p. 550 [1889].

warm liquid; the capillary pressure within the bubbles is added to the external pressure to be overcome; when the bubbles are small the capillary pressure becomes very considerable. The boiling of a liquid under ordinary conditions is, therefore, a constant process of oscillation between overheating and sudden formation of vapour, and these changes are accompanied by corresponding movements of temperature.

Fig. 24

Beckmann[1] has overcome these difficulties. The retardation of boiling, and the bumping consequent thereupon, were obviated by fixing (by the help of fusible glass) a small piece of stout platinum wire in the bottom of the small boiling-flask. The boiling then takes place exclusively from the piece of platinum, because of the very much greater thermal conductivity of the metal, and bumping is avoided entirely. To prevent local differences of temperature, the

[1] *Zeitschr. f. physikal. Chemie*, **4**, p. 539 [1889].

bottom of the boiling-flask was covered with a layer, which was a few centimetres deep, of coarsely powdered material such as glass beads or common garnets. The bubbles of vapour produced in the liquid pass through this layer, and thereby acquire a temperature which is so nearly equal to that of the liquid that no oscillations of temperature can be detected by the most delicate thermometer in a liquid boiling under these conditions.

Beckmann's apparatus is represented in fig. 24. The boiling-flask, shown at A, has three necks, and is furnished with the device for aiding boiling, s; one neck carries a thermometer; another, B, is attached to a reversed condenser; and the third, C, serves for the introduction of the substance. An experiment is conducted by placing a dry layer of garnets in A, adding a weighed quantity of the solvent, arranging the thermometer and condenser, and causing the liquid to boil quietly by a flame placed in a proper position. When the thermometer-reading has become constant, the temperature is noted, and a weighed quantity of the substance under examination is introduced by C. The temperature quickly rises, and after five to ten minutes it reaches its maximum-point, whereat it remains stationary.

The calculation is made most simply by taking into consideration the changes of pressures which are proportional to the changes of temperature. By applying the formula $\frac{p - p'}{p} = \frac{n}{N + n}$ to a solution of one molecule of the substance in 100 molecules of the solvent, the change of pressure is obtained to a hundredth part of its value, at the mean atmospheric pressure of 760 mm. One hundred times the temperature-difference which corresponds with this pressure-difference may be called the *molecular raising of boiling-point*. For instance, the value of this for ether is 28·44, i.e. one molecule of a substance dissolved in 99 molecules of ether raises the boiling-point of the latter by ·2844°. Putting S as the molecular raising of boiling-point,

the unknown molecular weight of a substance, g grams of which are dissolved in one molecular weight, i.e. in 74 grams, of ether, is obtained from the equation,

$$m = S\,\frac{g}{\Delta},$$

where Δ = the observed raising of boiling-point. The constant S may be referred to 100 grams, instead of to the molecular weight, of the solvent; the calculation is thus slightly simplified.

It is most convenient, in actual practice, to determine S empirically by conducting an experiment with a substance of known molecular weight.

The experiments which Beckmann conducted with the view of finding the molecular weights of iodine, phosphorus, and sulphur, may be taken as examples of the application of the method.[1] A solution of 1·065 grams iodine in 30·14 grams ether produced a rise of the boiling-point equal to ·296°. The quantity of iodine dissolved in 74 grams ether was therefore $\frac{1{\cdot}065}{30{\cdot}14} \times 74$; and, as S = 28·44, the molecular weight was,

$$m = 28{\cdot}44\,\frac{1{\cdot}065 \times 74}{30{\cdot}14 \times {\cdot}296} = 251.$$

The formula I_2 corresponds with the molecular weight 254.

The molecular raising of boiling-point for carbon disulphide was obtained as follows. Andrews found the heat of vaporisation of 1 gram CS_2 to be 86·72 cals., the molecular heat of vaporisation is therefore 6,593 cals. In the formula $\frac{dp}{dt} = \frac{\rho p}{2T^2}$, or $dt = \frac{2T^2}{\rho} \cdot \frac{dp}{p}$, T is equal to 273 + 46 = 319; and therefore $2T^2$ = 203,522; hence $dt = 30{\cdot}9\,\frac{dp}{p}$. For one molecule of the dissolved substance in 100 of the solvent, we have $\frac{dp}{p} = \frac{p - p'}{p} = \frac{n}{N + n}$ = ·01;

[1] *Zeitschr. f. physikal. Chemie*, 5, p. 76 [1890].

hence to obtain the one hundred times greater molecular raising of boiling-point, as defined above, we must put $\frac{dp}{p} = 1$; then S = 30·9.

Beckmann found that 1·4475 grams phosphorus in 54·65 grams carbon disulphide raised the boiling-point by ·486°. Hence,

$$m = 30{\cdot}9\frac{1{\cdot}4475 \times 76}{54{\cdot}65 \times {\cdot}486} = 128.$$

The molecular weight of phosphorus as determined from the vapour-density = 124. Hence the molecular weight of phosphorus dissolved in carbon disulphide is the same as that of gaseous phosphorus.

The values obtained for the molecular weight of sulphur in carbon disulphide varied between 245 and 315. The formula S_6, which had been generally adopted as the maximum molecular formula for sulphur, gives the molecular weight as 192; the numbers found by Beckmann point to the formula $S_8 = 256$. At any rate, these measurements show that the high specific gravity of sulphur vapour at a red heat is not caused only by deviations from the gaseous laws, but by the existence of complex molecules. Beckmann's results make it probable that the composition of these molecules is to be represented by the formula S_8 rather than by S_6; and experiments conducted recently by Hertz,[1] by the method dependent on the lowering of the freezing-point of a solution (see next Chapter), confirm the formula S_8.

10. **Theoretical considerations.**—The similarity between the laws of the diminution of vapour-pressure and those of osmotic pressure (both magnitudes are proportional to concentration, and are equal for equimolecular solutions) suggests the question whether these laws are not causally connected. That the connexion is indeed causal was first pointed out by van 't Hoff.[2] In place of the thermodyna-

[1] *Zeitschr. f. physikal. Chemie*, **6**, p. 358 [1890].

[2] *Ibid.* **1**, p. 494 [1887].

mical demonstration employed by van 't Hoff I give here a process of deduction, communicated by Arrhenius,[1] which is more easily followed.

Let there be a vessel of the shape of an inverted funnel, closed beneath by a semi-permeable membrane; let this vessel be filled with the solution L (fig. 25), and let it stand in another vessel, F, containing the solvent only; finally let the whole arrangement be covered by a bell-jar, within which a vacuum can be produced. The solution will be in equilibrium with the outer liquid when the pressure, which is exerted by the column $h\,G$, is equal to the osmotic pressure. Now the solvent evaporates at G, and the solution at h. The vapour-pressure of the solution at h must be equal to the pressure which the vapour of the solvent possesses at the same place, for if it were greater or less than this, liquid would either evaporate or condense at h; but in either case the pressure on the semi-permeable membrane would alter, and liquid would escape or would enter; this process would proceed endlessly; a perpetual motion would be produced, and this is impossible.

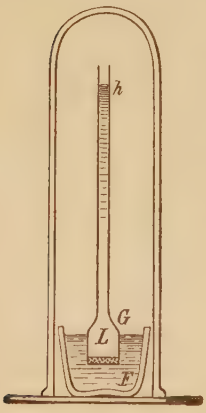


Fig. 25

The pressure which the vapour of the liquid F must exert at h is equal to the vapour-pressure of the solvent diminished by the weight of a column of vapour of the height $h\,G$. The vapour-pressure of the solution must be equal to this pressure.

Let us now assume the laws of osmotic pressure to be given. The solution contains n molecules of the dissolved substance and N molecules of the solvent. The osmotic pressure is equal to the pressure which the dissolved substance would exert were it present as gas in the given space; this pressure is given by the equation $p\,v = n\,\mathrm{R}\,\mathrm{T}$;

[1] *Zeitschr. f. physikal. Chemie*, 3, p. 115 [1889].

it is $p = \frac{n\,\mathrm{R\,T}}{v}$, where R = 84,700, and T is the absolute temperature. To find v, we pay regard to the fact that the N molecules of the solvent weigh M N, where M = molecular weight, and occupy the volume $\frac{\mathrm{M\,N}}{s}$, where s = specific gravity of the solvent. We thus obtain $p = \frac{n\,\mathrm{R\,T}\,s}{\mathrm{M\,N}}$. The height, h, of the column of solution, which corresponds with this pressure, is given by the equation $p = h\,s'$, where s' = specific gravity of the solution. If we regard solutions so dilute that their specific gravities do not differ substantially from that of the solvent, then s' may be replaced by s, and we have, $h = \frac{n\,\mathrm{R\,T}}{\mathrm{M\,N}}$. As MN is equal to the weight of the solvent in which are contained n molecular weights of the dissolved substance, the statement may be put thus:—the osmotic ascent is independent of the nature of the solvent for solutions of equal contents.

As regards the pressure which is exerted by a column of vapour of the height h, it was already shown that the vapour-pressure of the solution f' is smaller than that of the solvent. Putting the latter as f, then $f' = f - h\,d$, where d = density of the vapour. This value may also be found from the formula $p\,v = \mathrm{R\,T}$; p, which is the pressure of the vapour, is equal to f; and, as the formula is referred to one molecular weight of the vapour, d is equal to $\frac{\mathrm{M}}{v}$. Hence we obtain $d = \frac{f\,\mathrm{M}}{\mathrm{R\,T}}$.

Finally, by substituting in the equation $f' = f - dh$ the values $h = \frac{n\,\mathrm{R\,T}}{\mathrm{M\,N}}$ and $d = \frac{f\,\mathrm{M}}{\mathrm{R\,T}}$, we obtain $f' = f\left(1 - \frac{n}{\mathrm{N}}\right)$, or $\frac{f - f'}{f} = \frac{n}{\mathrm{N}}$.

The formula $\frac{f - f'}{f} = \frac{n}{\mathrm{N} + n}$ was obtained (p. 173) from the experiments of Raoult. The difference depends on the

fact that these experiments were made with solutions of limited concentrations, while the calculations are made for infinitely small concentrations; as a matter of fact, if n is very small compared with N, both formulæ give the same result.

11. **Limited concentrations.**—If the contents of a solution are not very small, the osmotic ascents become very considerable. The pressure in a normal solution which contains one gram-molecular weight of dissolved substance per litre amounts to about 22 atmospheres, and corresponds with an ascent of more than 220 metres. For such heights the pressure of the vapour can no longer be put as simply equal to $d\,h$, but the density d must be considered as variable with the height. We must, therefore, put $\mathrm{d}\,p = d.\,\mathrm{d}\,h$, and integrate from 0 to h. If $d = \frac{\mathrm{M}}{v}$ is replaced by the value $\frac{\mathrm{M}}{v} = \frac{\mathrm{M}p}{\mathrm{R\,T}}$, it follows that $\frac{\mathrm{R\,T}}{\mathrm{M}}.\ \frac{\mathrm{d}p}{p} = \mathrm{d}\,h$; or, by integrating, $h = \frac{\mathrm{R\,T}}{\mathrm{M}}\ l\ \frac{p_0}{p_h}$, where p_0 = the pressure for $h = 0$ —i.e. for the surface of the outer liquid—and p_h = the pressure at the height h in the osmometer: the first of these is the vapour-pressure, f, of the solvent, the second is the vapour-pressure, f', of the solution. By substituting this value for h in the equation which gives the height of the column of liquid, viz. $h = \frac{n\,\mathrm{R\,T}}{\mathrm{M\,N}}$, we have

$$l\,\frac{b}{f'} = \frac{n}{\mathrm{N}}.$$

Writing $l\,\frac{f}{f'}$ in the form $l\left(1 + \frac{f - f'}{f'}\right)$, and considering that $f - f'$ is small compared with f', the logarithm may be developed in a series

$$l\left(1 + \frac{f - f'}{f'}\right) = \frac{f - f'}{f'} - \tfrac{1}{2}\left(\frac{f - f'}{f'}\right)^2 + \ldots.$$

or, breaking off at the first term,

$$\frac{f-f'}{f'} = \frac{n}{N}$$

This expression may be transformed into

$$\frac{f-f'}{f} = \frac{n}{N+n}.$$

This, which is the empirical formula of Raoult, is thus deduced by general reasoning.

If the formula $l\frac{b}{f'} = \frac{n}{N}$ is applied to the measurements of Raoult, given on p. 172, a fair agreement is found for the numbers for dilute solutions, but the numbers for concentrated solutions depart much from the calculated numbers. For example, the solutions of turpentine in ether give the following results :—

$\frac{n}{N}$	$l\frac{p}{p'}$	$\frac{n}{N}$	$l\frac{p}{p'}$
·0627	·0619	·5504	·391
·1377	·1278	·9194	·576
·3055	·2473	1·817	·865

The formula cannot be expected to hold good for more concentrated solutions, to which the assumptions made in deducing the formula are not applicable. This formula, however, gives better results than that of Raoult for solutions where $\frac{n}{N} < \cdot 1$; as the calculation is simple enough, it may be employed for such solutions in place of Raoult's formula.

12. **Solutions of salts.**—The laws which have been developed for solutions of indifferent substances in various solvents do not apply to solutions of salts in water. A solution of the composition $KCl + 100\,H_2O$, instead of showing a lowering of vapour-pressure of ·01, as required by the law, shows a lowering about double this. The

deviations are still greater for salts of the type of barium chloride; this is seen by the numbers given on p. 162. Deviations of this kind are not exhibited by all aqueous solutions. Solutions in water of indifferent substances, such as urea, show normal diminutions. Walker found ·0091, in place of ·01, for $CON_2H_4 + 100\ H_2O$; and Raoult showed that aqueous solutions of indifferent substances obey the law (p. 170).

Moreover, these deviations are not a constant peculiarity of salt-solutions. Solutions of salts in alcohol behave like all other substances and give normal diminutions of vapour-pressure. Raoult,[1] who made a special investigation of this matter, gave the following table :—

Substance	Formula	Lowering of vapour-pressure
Sodium perchlorate	$NaClO_4$	·0098
Potassium acetate	$KC_2O_2H_3$	·0100
Sodium ethylate	$C_2H_5ONa \cdot 3\,C_2H_6O$	·0105
Lithium chloride	$LiCl \cdot 5\,C_2H_6O$	·0104
Lithium bromide	$LiBr \cdot 5\,C_2H_6O$	·0104
Potassium sulphocyanide	$KSCN$	·0105
Calcium nitrate	CaN_2O_6	·0099
Calcium chloride	$CaCl_2 \cdot 3\,C_2H_6O$	·0099
Mercuric cyanide	HgC_2N_2	·0110
Thymol	$C_{10}H_{14}O$	·0106
Picric acid	$C_6H_3N_3O_7$	·0103
Nitrobenzene	$C_6H_5NO_2$	·0097
Ethyl salicylate	$C_9H_{10}O_3$	·0097
Ethyl benzoate	$C_9H_{10}O_2$	·0094
Diphenylamine	$C_{12}H_{11}N$	·0100
Naphthalene	$C_{10}H_8$	·0091

The last column contains the molecular lowerings of vapour-pressures, for the proportion 1 : 100 molecules; they do not deviate much on either side from the theoretical value ·01; it is especially to be noted that the salts do not behave at all differently from the organic compounds which are placed towards the end of the table.

The especial peculiarity under consideration is evidently confined to aqueous solutions of salts (to which may be added

[1] *Compt. rend.* **107**, p. 442 [1888].

the strong acids and bases). The behaviour of these substances is as if the solutions contained a considerably greater number of molecules of the dissolved substances than corresponds with their formulæ, i.e. *as if the substances in solution were broken up into smaller molecules.*

The solutions which exhibit these deviations from the laws of vapour-pressure possess another characteristic peculiarity: they, and only they, are good conductors of the electric current, and they conduct electrolytically, i.e. the movement of electricity is accompanied by a movement of ponderable particles which are called *ions*. By ions is understood the constituent parts of salts, acids, and bases, viz. on one side, the metals, the metal-like radicles such as NH_4, and hydrogen, and on the other side, the halogens, the acidic radicles such as NO_3 or SO_4, and hydroxyl. The positive electricity moves along with the first-named, or positive, ions; while the negative electricity accompanies the second, or negative, ions. The consideration of these relations, along with the deviations from the laws of vapour-pressure, leads to the supposition that *in their aqueous solutions the substances in questions*, i.e. *the electrolytes, are already separated for the most part into their ions.* This conclusion was arrived at by Arrhenius;[1] the conclusion, it must be admitted, is, to some extent, opposed to the views which generally prevail, but it is in agreement with quite a remarkable number of facts.[2]

The relations in question are similar to those which are observed in the cases of so-called 'abnormal vapour-densities.' The same difficulties which formerly prevented chemists from representing to themselves the existence of uncombined ammonia and hydrochloric acid in the vapour of sal ammoniac, now militate against the supposition that, e.g. potassium and chlorine can exist side by side in a solution of potassium chloride. I do not attempt here to

[1] *Zeitschr. f. physikal. Chemie*, 1, p. 631 [1887].

[2] The supposition in question is fully considered in a later chapter of the *Lehrbuch.—Translator.*

explain these difficulties, which can be shown to be erroneous; we are concerned at present with the hypothetical expression that the aqueous solutions of electrolytes behave as if the electrolytes were separated into their ions. The amount of this separation can easily be calculated by comparing the observed lowering of vapour-pressure with that calculated on the assumption of an unchanged molecular condition. It has already been remarked that the measurements of the diminutions of vapour-pressure are not very accurate. As we shall find hereafter a much more accurate method by which more trustworthy results can be obtained, we shall defer calculations of this kind until then.

Meanwhile, the results of a very extended series of measurements of the vapour-pressures of salt-solutions at 100°, made by G. Tammann,[1] are given here, as a foundation for further advances. The method consisted in placing the solution in a U tube; one limb of this tube was closed, mercury was placed in the bend of the tube, and the open end was connected with a manometer and an air-pump. The U tube was heated in the vapour of boiling water, and the decrease of pressure required to make possible the formation of vapour at this temperature was measured. The numbers in the following table represent the diminutions of vapour-pressure, in millimetres, which were caused by the solution of n molecular weights, in grams, of the salts in 1,000 grams of water.

[1] *Mém. Acad. Pétersb.* **35**, No. 9 [1887].

Notes to Table, pp. 191–193

30, sodium phenolsulphonate (probably *para-*); 41, *normal* potassium butyrate; 42, potassium isobutyrate; 48 and 49, the corresponding sodium salts; 71, glycolic acid; 72, lactic acid; 73, succinic acid; 74, malic acid; 75, tartaric acid; 76, racemic acid; 77, citric acid; 93, sodium paratungstate; 104, potassium malonate; 105, tartar-emetic; 106, potassium succinate; 108 and 109, potassium and sodium tartrate; 110 and 111, potassium and sodium citrate.

		$n=0.5$	1	2	3	4	5	6	8	10
1	KCl	12·2	24·4	48·8	74·1	100·9	128·5	152·2	—	—
2	KSCN	10·8	22·8	48·8	76·0	100·5	128·5	152·8	200·2	241·0
3	KBr	12·0	24·2	50·8	76·5	105·5	132·8	160·0	—	—
4	KI	12·5	25·3	52·2	82·6	112·2	141·5	171·8	225·5	278·5
5	KF	10·6	22·3	46·0	75·0	106·0	136·5	166·8	233·0	—
6	NaCl	12·3	25·2	52·1	80·0	111·0	143·0	176·5	—	—
7	NaSCN	11·6	24·6	55·7	89·2	122·0	156·2	195·0	256·2	314·0
8	NaBr	12·6	25·9	57·0	89·2	124·2	159·5	197·5	268·0	—
9	NaI	12·1	25·6	60·2	99·5	136·7	177·5	221·0	301·5	370·0
10	NaF	11·4	23·0	—	—	—	—	—	—	—
11	NH_4Cl	12·0	23·7	45·1	69·3	94·2	118·5	138·2	179·0	213·8
12	NH_4SCN	10·8	22·0	46·0	68·6	93·0	117·5	140·0	179·5	218·0
13	NH_4Br	11·9	23·9	48·8	74·1	99·4	121·5	145·5	190·2	228·5
14	NH_4I	12·5	25·1	49·8	78·5	104·5	132·3	156·0	200·0	243·5
15	LiCl	12·1	25·5	57·1	95·0	132·5	175·5	219·5	311·5	393·5
16	LiBr	12·2	26·2	60·0	97·0	140·0	186·3	241·5	341·5	438·0
17	LiI	13·6	28·6	64·7	105·2	154·5	206·0	264·0	357·0	445·0
18	RbCl	12·2	24·6	50·0	76·5	101·0	128·5	156·0	203·5	247·0
19	KNO_2	11·1	22·8	44·8	67·0	90·0	110·5	130·7	167·0	198·8
20	KNO_3	10·3	21·1	40·1	57·6	74·5	88·2	102·1	126·3	148·0
21	$KClO_3$	10·6	21·6	42·8	62·1	80·0	—	—	—	—
22	$KClO_4$	11·5	22·3	—	—	—	—	—	—	—
23	$KBrO_3$	10·9	22·4	45·0	—	—	—	—	—	—
24	$KHSO_4$	10·9	21·9	43·3	65·3	85·5	107·8	129·2	170·0	—
25	$NaNO_2$	11·6	24·4	50·0	75·0	98·2	122·5	146·5	189·0	226·2
26	$NaNO_3$	10·6	22·5	46·2	68·1	90·3	111·5	131·7	167·8	198·8
27	$NaClO_3$	10·5	23·0	48·4	73·5	98·5	123·3	147·5	196·5	223·5
28	$NaBrO_3$	12·1	25·0	54·1	81·3	108·8	136·0	—	—	—
29	$NaHSO_4$	10·9	22·1	47·3	75·0	100·2	126·1	148·5	189·7	231·4
30	$C_6H_5O{\cdot}SO_3Na$	11·8	22·6	49·8	75·5	104·5	—	—	—	—
31	NH_4NO_3	12·8	22·0	42·1	62·7	82·9	103·8	121·0	152·2	180·0
32	$NH_4{\cdot}HSO_4$	11·5	22·0	46·8	71·0	94·5	118·0	139·0	181·2	218·0
33	NH_4BF_4	10·5	22·2	45·0	67·0	93·5	—	—	—	—
34	$LiNO_3$	12·2	25·9	55·7	88·9	122·2	155·1	188·0	253·4	309·2
35	$LiHSO_4$	12·8	27·0	57·0	93·0	130·0	168·0	—	—	—
36	$RbNO_3$	10·9	22·1	42·1	58·2	73·8	89·2	—	—	—
37	$RbHSO_4$	10·9	21·9	43·0	63·6	83·8	104·0	—	—	—
38	HCO_2K	11·6	23·6	59·0	77·6	104·2	132·0	160·0	210·0	255·0
39	CH_3CO_2K	12·4	24·0	54·6	86·0	119·0	152·0	186·2	250·0	307·0
40	$C_2H_5CO_2K$	12·3	24·0	53·0	84·8	116·8	148·0	181·0	234·0	288·4
41	$C_3H_7CO_2K$	12·4	24·0	54·4	84·0	113·4	141·0	169·0	219·0	266·0
42	i-$C_3H_7CO_2K$	12·2	24·0	52·2	80·4	110·0	139·0	167·4	218·0	266·0
43	$C_4H_9CO_2K$	11·5	22·0	49·6	74·4	99·8	122·4	145·6	190·0	230·6
44	$C_5H_{11}CO_2K$	12·2	22·0	48·2	72·4	96·0	118·8	142·0	—	—
45	HCO_2Na	12·9	24·1	48·2	77·6	102·2	127·8	152·0	198·0	239·4
46	CH_3CO_2Na	11·5	26·0	52·0	83·0	113·4	143·0	173·0	227·0	278·0
47	$C_2H_5CO_2Na$	10·9	22·6	46·2	71·4	97·4	122·2	146·0	189·0	232·0
48	$C_3H_7CO_2Na$	12·5	26·0	53·0	81·6	108·2	131·0	153·6	193·0	230·0
49	i-$C_3H_7CO_2Na$	11·8	24·0	52·0	81·6	108·4	133·4	158·0	200·4	237·0
50	$C_4H_9CO_2Na$	11·4	24·0	51·0	73·8	96·0	114·8	132·0	164·0	199·0
51	$C_5H_{11}CO_2Na$	11·2	23·0	44·2	65·0	86·0	103·0	—	—	—
52	NH_4OHCl	11·2	22·0	45·0	69·0	90·0	110·5	—	—	—
53	$N(CH_3)_3Cl$	11·1	22·0	49·0	76·2	106·1	134·9	163·5	219·3	275·2
54	$N(CH_3)_2HCl$	7·0	—	—	—	—	—	—	—	—
55	$N(CH_3)_2H_2Cl$	9·6	19·5	41·8	65·0	91·8	116·3	142·0	186·8	230·3
56	$N(CH_3)H_3Cl$	9·4	20·0	43·0	68·4	92·0	114·3	137·0	180·0	218·0
57	$N(C_2H_5)_3HCl$	6·5	—	—	—	—	—	—	—	—
58	$N(C_2H_5)_2H_2Cl$	7·9	—	—	—	—	—	—	—	—
59	$N(C_2H_5)H_3Cl$	9·9	15·8	39·0	62·7	85·0	107·9	129·1	—	—
60	CN_3H_4Cl	11·6	22·2	42·0	61·8	80·9	99·5	118·0	152·0	185·0
61	$N(C_6H_5)H_3Cl$	10·6	20·4	39·0	57·0	73·8	88·6	101·0	—	—
62	$N(C_6H_5)H_3NO_3$	9·9	18·5	34·8	48·5	60·0	71·5	82·4	102·8	—
63	LiOH	15·9	37·4	78·1	—	—	—	—	—	—
64	KOH	15·0	29·5	64·0	99·2	140·0	181·8	223·0	309·5	387·8
65	NaOH	11·8	22·8	48·2	77·3	107·5	139·1	172·5	243·3	314·0
66	$Ba(OH)_2$	12·3	22·5	39·0	—	—	—	—	—	—
67	H_2SO_4	12·9	26·5	62·8	104·0	148·0	198·4	247·0	343·2	—
68	H_3AsO_4	7·3	15·0	30·2	46·4	64·9	—	—	—	—
69	H_3PO_4	6·6	14·0	28·6	45·2	62·0	81·5	103·0	146·9	189·5
70	H_3BO_3	6·0	12·3	25·1	38·0	51·0	—	—	—	—
71	$CH_2OH{\cdot}CO_2H$	7·0	14·0	26·5	39·2	50·0	—	—	—	—
72	$C_2H_4(OH){\cdot}CO_2H$	6·5	12·4	24·0	34·3	44·7	55·0	65·6	88·0	110·6
73	$C_2H_4(CO_2H)_2$	6·2	12·4	24·8	36·7	48·5	59·7	71·2	94·1	—

		$n=0·5$	1	2	3	4	5	6	8	10
74	$C_2H_3OH(CO_2H)_2$	6·6	13·5	27·4	44·0	59·7	75·8	91·6	124·9	166·5
75	$C_2H_2(OH)_2(CO_2H)_2$	6·9	14·3	30·0	47·7	66·8	86·4	103·1	135·0	167·8
76	$C_2H_2(OH)_2(CO_2H)_2$	7·8	15·4	32·3	48·3	66·9	86·5	106·2	151·0	—
77	$C_2H_4(OH)(CO_2H)_2$	7·9	15·0	31·8	50·0	71·1	92·8	—	—	—
78	K_2WO_4	13·9	33·0	75·0	123·8	175·4	226·4	—	—	—
79	K_2MoO_4	14·1	31·6	70·0	117·6	164·6	213·0	—	—	—
80	K_2CrO_4	16·2	29·5	60·0	—	—	—	—	—	—
81	K_2SO_4	13·7	26·7	—	—	—	—	—	—	—
82	$K_2S_2O_6$	12·1	24·0	46·0	—	—	—	—	—	—
83	$K_2S_2O_3$	13·7	26·0	53·5	83·0	113·8	144·6	175·5	235·0	—
84	K_2CO_3	14·4	31·0	68·3	105·5	152·0	209·0	258·5	350·0	—
85	$K_4Fe(CN)_6$	16·6	37·0	—	—	—	—	—	—	—
86	Na_2WO_4	14·8	33·6	71·6	115·7	162·6	—	—	—	—
87	Na_2MoO_4	16·6	33·2	70·8	119·0	169·2	216·0	—	—	—
88	Na_2CrO_4	14·5	30·0	65·8	105·0	146·0	—	—	—	—
89	Na_2SO_4	12·6	25·0	48·9	74·2	—	—	—	—	—
90	$Na_2S_2O_6$	13·5	29·5	63·5	100·5	—	—	—	—	—
91	$Na_2S_2O_3$	14·1	29·5	62·1	97·0	137·0	177·7	215·6	278·0	—
92	Na_2CO_3	14·3	27·3	53·5	80·2	111·0	—	—	—	—
93	$Na_2W_4O_{13}$	12·1	20·3	51·8	106·5	—	—	—	—	—
94	$Na_2B_4O_7$	20·7	33·8	54·0	—	—	—	—	—	—
95	$(NH_4)_2SO_4$	11·0	24·0	46·5	69·5	93·0	117·0	141·8	—	—
96	$(NH_4)_2S_2O_6$	13·2	28·2	59·0	91·0	120·0	—	—	—	—
97	$(NH_4)_2SiF_6$	11·5	25·0	44·5	—	—	—	—	—	—
98	Li_2CrO_4	16·4	32·6	74·0	120·0	171·0	—	—	—	—
99	Li_2SO_4	13·3	28·1	56·8	89·0	—	—	—	—	—
100	$Li_2S_2O_6$	15·4	36·5	91·0	158·0	225·0	—	—	—	—
101	Li_2SiF_6	15·4	34·0	70·0	106·0	—	—	—	—	—
102	Rb_2SO_4	14·6	28·3	57·8	86·8	—	—	—	—	—
103	$C_2O_4K_2$	13·9	28·3	59·8	94·2	131·0	—	—	—	—
104	$CH_2(CO_2K)_2$	13·4	—	—	—	—	—	—	—	—
105	$C_4H_4KSbO_7$	27·1	—	—	—	—	—	—	—	—
106	$C_2H_4(CO_2K)_2$	16·7	36·0	80·5	130·1	180·9	230·5	—	—	—
107	$C_2H_4(CO_2Na)_2$	16·7	34·5	76·2	122·5	165·6	—	—	—	—
108	$C_4H_4O_2(CO_2K)_2$	14·6	29·5	60·1	92·0	126·0	157·9	188·0	—	—
109	$C_2H_3O_2(CO_2Na)_2$	14·7	28·7	58·0	83·0	110·0	132·0	155·0	—	—
110	$C_3H_5OH(CO_2K)_3$	16·9	37·9	89·7	140·5	205·4	258·2	—	—	—
111	$C_3H_5OH(CO_2Na)_3$	16·2	35·7	78·0	119·2	—	—	—	—	—
112	KH_2PO_4	10·2	19·5	33·3	47·8	60·5	73·1	85·2	—	—
113	KH_2AsO_4	10·9	20·0	37·2	54·0	69·5	—	—	—	—
114	NaH_2PO_4	10·5	20·0	36·5	51·7	66·8	82·0	96·5	126·7	157·1
115	NaH_2AsO_4	11·3	20·6	38·8	57·0	74·9	92·8	—	—	—
116	Na_2HPO_4	12·1	23·5	43·0	60·0	78·7	99·8	122·1	—	—
117	Na_2HAsO_4	14·3	26·5	50·7	75·8	—	—	—	—	—
118	Na_3PO_4	16·5	30·0	52·5	—	—	—	—	—	—
119	$Na_4P_2O_7$	13·2	22·0	—	—	—	—	—	—	—
120	$(NaPO_3)_3$	17·1	36·5	—	—	—	—	—	—	—
121	$(NaPO_3)_6$	11·6	—	—	—	—	—	—	—	—
122	$AlCl_3$	22·5	61·0	179·0	318·0	—	—	—	—	—
123	$CeCl_3$	21·6	52·8	137·0	229·0	—	—	—	—	—
124	$BeBr_2$	17·8	45·0	125·2	227·5	329·0	—	—	—	—
125	$BeCl_2$	17·4	43·2	110·5	195·5	291·1	368·7	—	—	—
126	BeN_2O_6	16·5	—	—	—	—	—	—	—	—
127	$MgBr_2$	17·9	44·0	115·8	205·3	298·5	—	—	—	—
128	$MgCl_2$	16·8	39·0	100·5	183·3	277·0	377·0	—	—	—
129	MgN_2O_6	17·6	42·0	101·0	174·8	—	—	—	—	—
130	$CaBr_2$	17·7	44·2	105·8	191·0	283·3	368·5	—	—	—
131	$CaCl_2$	17·0	39·8	95·3	166·6	241·5	319·5	—	—	—
132	CaN_2O_6	16·4	34·8	74·6	139·3	161·7	205·4	—	—	—
133	$SrBr_2$	17·8	42·0	101·1	179·0	267·0	—	—	—	—
134	$SrCl_2$	16·8	38·8	91·4	156·8	223·3	281·5	—	—	—
135	SrN_2O_6	15·8	31·0	64·0	97·4	131·4	—	—	—	—
136	$BaBr_2$	16·8	38·8	91·4	150·0	204·7	—	—	—	—
137	$BaCl_2$	16·4	36·7	77·6	—	—	—	—	—	—
138	$BaCl_2O_6$	15·8	33·3	70·5	108·2	—	—	—	—	—
139	BaN_2O_6	13·5	27·0	—	—	—	—	—	—	—
140	$Ba(BF_4)_2$	17·5	—	—	—	—	—	—	—	—
141	$(C_6H_5SO_3)_4Ba$	14·2	—	—	—	—	—	—	—	—
142	$(C_6H_5O\cdot SO_3)_2Ba$	14·5	—	—	—	—	—	—	—	—
143	$(CH_3CO_2)_2Ba$	14·6	—	—	—	—	—	—	—	—
144	$(C_2H_5CO_2)_2Ba$	13·9	—	—	—	—	—	—	—	—
145	$(C_2H_5CO_2)_2Ca$	13·8	—	—	—	—	—	—	—	—
146	$(C_2H_5OCO_2)_2Ca$	10·4	—	—	—	—	—	—	—	—

		$n=0·5$	1	2	3	4	5	6	8	10
147	$NiCl_2$	16·1	37·0	86·7	147·0	212·8	—	—	—	—
148	NiN_2O_6	16·1	37·3	91·3	156·2	235·0	—	—	—	—
149	$CoCl_2$	15·0	34·8	83·0	136·0	186·4	—	—	—	—
150	CoN_2O_6	17·3	39·2	89·0	152·0	218·7	282·0	332·0	—	—
151	$MnCl_2$	15·0	34·0	76·0	122·3	167·0	209·0	—	—	—
152	$FeCl_2$	16·7	36·8	86·3	139·0	195·0	247·2	298·0	—	—
153	$ZnCl_2$	9·2	18·7	46·2	75·0	107·0	153·0	195·0	—	—
154	ZnN_2O_6	16·6	39·0	93·5	157·5	223·8	—	—	—	—
155	$CdCl_2$	9·6	18·8	36·7	57·0	77·3	99·0	—	—	—
156	$CdBr_2$	8·6	17·8	36·7	55·7	80·0	—	—	—	—
157	CdI_2	7·6	14·8	33·5	52·7	—	—	—	—	—
158	CdN_2O_6	15·9	36·1	78·0	122·2	—	—	—	—	—
159	$CdCl_2O_6$	17·5	—	—	—	—	—	—	—	—
160	$UO_2N_2O_6$	18·4	—	—	—	—	—	—	—	—
161	HgC_2N_2	6·4	12·1	—	—	—	—	—	—	—
162	PbN_2O_6	12·3	23·5	45·0	63·0	—	—	—	—	—
163	$(CH_3CO_2)_2Pb$	8·0	14·1	23·3	33·0	41·8	50·2	59·3	—	—
164	CaS_2O_6	9·9	23·0	56·0	106·0	—	—	—	—	—
165	SrS_2O_6	7·2	10·3	47·0	—	—	—	—	—	—
166	BaS_2O_6	6·6	15·4	34·4	—	—	—	—	—	—
167	$Al_2(SO_4)_3$	12·8	36·5	—	—	—	—	—	—	—
168	$BeSO_4$	5·3	12·5	27·5	52·0	85·0	123·0	161·0	—	—
169	$MgSO_4$	6·5	12·0	24·5	47·5	—	—	—	—	—
170	$MgH_2(SO_4)_2$	18·3	46·0	116·0	—	—	—	—	—	—
171	$FeSO_4$	5·8	10·7	24·0	42·4	—	—	—	—	—
172	$CoSO_4$	5·5	10·7	22·9	45·5	—	—	—	—	—
173	$NiSO_4$	5·0	10·2	21·5	—	—	—	—	—	—
174	$ZnSO_4$	4·9	10·4	21·5	42·1	66·2	—	—	—	—
175	$CdSO_4$	4·1	8·9	18·1	—	—	—	—	—	—
176	$CuSO_4$	6·0	12·5	27·7	48·5	—	—	—	—	—
177	$MnSO_4$	6·0	10·5	21·0	—	—	—	—	—	—
178	UO_2SO_4	4·1	10·4	23·2	40·8	64·0	—	—	—	—
179	$UO_2H_2(SO_4)_2$	13·3	44·0	109·0	—	—	—	—	—	—
180	$Al_2(SO_4)_3·(NH_4)_2SO_4$	24·1	56·0	—	—	—	—	—	—	—

13. **Vapour-pressures of amalgams.**—Although the general validity of the law of vapour-pressure might lead one to suppose that it would apply to solutions of metals in metals, yet the verification of this expectation by W. Ramsay[1] possesses an especial interest, inasmuch as the metals differ sufficiently from other substances in their properties to make the application of the law in question appear somewhat doubtful. The experiments were made with mercury. Two U tubes were used, each with one short closed limb and one long open limb; one tube was filled with the amalgam to be examined, and the other with pure mercury. The two tubes were placed side by side in a bath of mercury-vapour, and the difference between the heights of the metals was read off. In every case there was noticed a diminution of vapour-pressure. The following

[1] *Chem. Soc. Journal*, Trans. 1889, p. 521.

table gives the molecular weights calculated from the observed lowerings of vapour-pressure :—

Metal	Molecular weight found	Atomic weight
Li	7·1	7·02
Na	21·6– 15·1	23·04
K	30·2– 29·1	39·1
Ca	19·1	40·1
Ba	75·7	137·0
Mg	24·0– 21·5	24·3
Zn	70·1– 65·4	65·4
Cd	99·7–103·8	112·1
Al	33·1– 36·7	27·0
Ga	69·7	69·9
Tl	163·6–197·6	204·2
Sn	117·4–149·5	119·1
Pb	200–250	206·9
Sb	136–301	120·0
Bi	214–232	208·0
Mn	55·5	55·0
Ag	112·4	107·9
Au	207·4–208·1	197·2

A comparison of the two columns shows that the metals tend to form the simplest molecules possible, i.e. molecules consisting of single atoms. The same thing has been noticed for those metals which have been gasified. The numbers found for the molecular weights of calcium and barium are very noteworthy; they are about half as large as the atomic weights; the number found for potassium is also much smaller than the atomic weight. No satisfactory explanation of these numbers has yet been found. The molecular weights of most of the other metals, when in solution, are the same as their atomic weights; aluminium, and, more markedly, antimony, show a tendency to form complex molecules. This behaviour agrees with that of these metals in the gaseous state.

14. **Vapour-pressures of solutions of volatile liquids.**— The evaporation of three kinds of pairs of liquids was considered in Chapter III.; to which of these cases the vapour-pressure of a mixture of liquids belongs, depends upon the nature of both constituents, and cannot be determined beforehand by the means at present in our hands.

But an approximate law can be deduced, by a method put forward by M. Planck [1] for the case that one of the liquids is present in considerably smaller quantity than the other, that is, for the case of a dilute solution.

We consider a solution wherein N molecules of the solvent are present to n molecules of the dissolved substance, and which has been partially vaporised so that the vapour contains n' molecules of the dissolved substance to N′ molecules of the solvent. We then define the '*numerical concentration*' as

$$c = \frac{n}{n + \mathrm{N}}, \; c' = \frac{n'}{n' + \mathrm{N}'},$$

where the undashed letters refer to the solution and the dashed letters to the vapour.

Thermodynamical considerations [2] lead to the equations

$$c - c' = l\,\mathrm{K}$$

$$l\,\frac{c}{c'} = l\,\mathrm{K}_1,$$

where l is the natural logarithm, and K and K_1 are two functions of pressure and temperature, which are not themselves known, but for which the following relations hold:—

$$\frac{d\,(l\,\mathrm{K})}{d\,\mathrm{T}} = \frac{\mathrm{Q}}{\mathrm{R}\,\mathrm{T}^2}, \text{ and } \frac{d\,(l\,\mathrm{K}_1)}{dp} = -\frac{\mathrm{V}}{\mathrm{R}\,\mathrm{T}},$$

where Q = heat of evaporation, V = volume-change accompanying evaporation of the solvent, respectively to the dissolved substance, for specified values of T and p.

If p_0 is the vapour-pressure of the pure solvent, l K may be developed in a series

$$l\,\mathrm{K} = l\,\mathrm{K}_0 - (p - p_0)\left(\frac{d\,l\,\mathrm{K}}{d\,p}\right)_0 + \ldots .$$

which may be stopped at the first member, inasmuch as

[1] *Zeitschr. f. physikal. Chemie*, **2**, p. 405 [1888].
[2] *Wied. Ann.* **32**, p. 489 [1887].

$p - p_0$ is small compared with p. Substituting the value for $\frac{d\,l\,K}{d\,p}$, we have

$$c - c' = l\,K_0 - (p - p_0)\frac{V_0}{RT}.$$

Bringing in the gaseous law $p\,v = R\,T$, we must put $v = V_0 = \frac{RT}{p_0}$, and we obtain

$$c - c' = l\,K_0 - \frac{p - p_0}{p_0}.$$

If the equation is applied to the pure solvent, $c = c' = 0$, and $p = p_0$, therefore $l\,K_0 = 0$, and hence

$$c - c' = \frac{p_0 - p}{p_0},$$

i.e. the relative lowering of vapour-pressure is equal to the difference between the concentrations of the dissolved substance in the liquid and in the vapour.

The equation shows that $c - c'$ and $p_0 - p$ have always the same sign. If $c - c'$ is positive, then $p_0 > p$, i.e. the concentration in the vapour is less than in the liquid, and therefore the vapour-pressure of the solution is smaller than that of the pure solvent, and *vice versâ*. If $c = c'$, then $p_0 = p$, i.e. when the solution evaporates without change its vapour-pressure is equal to that of the pure solvent. These statements had been put forward already by Konowaloff.

If the dissolved substance is not volatile, then $c' = 0$, and therefore $c = \frac{p_0 - p}{p_0}$; or $\frac{n}{N + n} = \frac{p_0 - p}{p_0}$, in accordance with the law mentioned before. The first equation may be developed in the same way for powers of $T - T_0$. Carrying out the calculation in quite the corresponding way, one obtains,

$$c - c' = (T - T_0)\frac{Q}{R\,T_0^{\,2}}.$$

The same conclusions may be drawn in this case: $c - c'$ has the same sign as $T - T_0$, so that for $c \gtreqless c'$, also $T \gtreqless T_0$. It should be noted especially that a dilute solution which can distil undecomposed has the same boiling-point as the solvent. If $c' = 0$, i.e. if the dissolved substance is not volatile, then $c = (T - T_0)\frac{Q}{R T^2}$, which is the equation used in Beckmann's boiling method (p. 178).

The second formula given above may be treated in a similar way. By differentiating, $l\frac{c'}{c} = l_K$, and then $d\,l\frac{c'}{c} = d\,l_{K_1}$, and by using the formula on p. 195, the complete differential is obtained,

$$d\,l\frac{c'}{c} = \frac{Q_1}{R T^2}\,d\,T - \frac{V_1}{R T}\,d\,p.$$

This formula cannot be applied in the present state of knowledge. For a homogeneous liquid, or generally for a liquid such that $\frac{c'}{c}$ remains constant, there is obtained $\frac{Q_1}{R T^2}\,d\,T = \frac{V_1}{R T}\,d\,p$, or the known equation,

$$\frac{d\,p}{d\,T} = \frac{Q}{T V_1}.$$

The equations of Planck have been subjected to experimental proof by A. Winkelmann.[1] If the concentration, c, and the vapour-pressure, p, of the solution are known, then knowing the vapour-pressure of the pure solvent, p_0, the concentration of the vapour, c', can be calculated by the equation $c - c' = \frac{p_0 - p}{p_0}$. Winkelmann determined the concentration of the vapour experimentally, by condensing the vapour and examining the few drops of liquid so obtained by Abbe's refractometer. The results confirmed the

[1] *Wied. Ann.* **39**, p. 1 [1890].

theory on the whole, but some considerable deviations were noticed in particular cases, which may have been due to the fact that Winkelmann did not determine directly the vapour-pressures of the solutions he used, but employed observations made by Konowaloff.

CHAPTER VIII

FREEZING-POINTS OF SOLUTIONS

1. Historical.—The laws which express the effect of dissolved substances on the temperature of solidification of solvents were made known by Blagden,[1] quite a hundred years ago. Blagden showed that the depressions of the freezing-points of aqueous solutions of the same substance below the freezing-point of water were proportional to the quantities of substance in solution. Blagden also found that two substances present together acted so that the lowering of the freezing-point of the common solution was equal to the sum of the effects which would be exerted were the substances present each by itself. Further experiments brought to light deviations from the first law, in the sense that the lowering of the freezing-points of solutions containing large quantities of dissolved substance increased more rapidly than the quantity of substance in solution. Deviations of this kind were observed for potassium carbonate, sulphuric acid, &c. Blagden also observed that the lowering of freezing-point sometimes increased more slowly than the contents of the solution; but he gave this result only with reservation. Although the work of Blagden was remarkably accurate, for the time, yet it fell into oblivion. Rüdorff made again the same discovery in 1861. It was only in 1871 that Coppet drew attention to the older investigations.

Before proceeding to consider the investigations in detail, an answer must be found to the preliminary question whether ice only, or ice and salt together, separate

[1] *Phil. Trans.* **78**, p. 277 [1788].

from solutions of salts. The fact, which has long been known, that melted sea-ice gives drinkable water, is in favour of the first alternative; and the question has been answered in this sense in a discussion between Rüdorff and Dufour. Rüdorff showed especially, by many experiments of different kinds, that the trace of salt which is generally found in ice that separates from a salt-solution is not present as solid salt, but as mechanically enclosed liquid; for instance, he showed that a solution of magnesium platino-cyanide, which solution is colourless, yielded colourless ice, whereas the colour of the solid platino-cyanide is intensely deep red. Fritzsche[1] obtained similar results; by freezing coloured solutions he got colourless ice, while the colouring material remained in solution. The same thing was alluded to in the older observations of Kries,[2] but nothing specially belonging to the subject is to be found in the work of this observer.

2. **Investigations of Rüdorff.**—Without being aware of Blagden's work, Rüdorff[3] took up the same problem in Magnus's laboratory, and arrived at the conclusion that the lowering of the freezing-point is proportional to the quantity of salt in solution. I give the following as examples of his observations (M = salt-contents of the solution):—

KCl			$NaNO_3$			K_2CO_3		
M	t	$\frac{t}{M}$	M	t	$\frac{t}{M}$	M	t	$\frac{t}{M}$
1	−0·45°	−·450	1	−0·4°	−·400	1·41	−0·45°	−·319
2	−0·9	−·450	2	−0·75	−·375	3·06	−0·95	−·310
4	−1·8	−·450	4	−1·5	−·391	5·29	−1·7	−·321
6	−2·65	−·442	6	−2·35	−·362	7·715	−2·45	−·318
8	−3·55	−·443	8	−2·9	−·360	12·20	−3·9	−·319
10	−4·4	−·440	10	−3·6	−·363	14·86	−4·7	−·316
12	−5·35	−·446	12	−4·35	−·350			
			14	−4·9	−·355			−·317
		−·446	16	−5·65				
					−·370			

[1] *Petersb. Akad. Bull.* **6**, pp. 385, 495 [1863].
[2] *Schweigger's Journ.* **11**, p. 26 [1814].
[3] *Pogg.* **114**, p. 63 [1861]; **116**, p. 55 [1862]; **145**, p. 599 [1871].

The proportion between the lowering of temperature and the quantity of salt in 100 parts of water, $\frac{t}{M}$, is seen to be nearly constant. This is not, however, always the case; for instance, the quotient in question increases with increase of the contents of the solution when calcium chloride is the salt used.

$CaCl_2$			$CaCl_2.6H_2O$		
M	t	$\frac{t}{M}$	M	t	$\frac{t}{M}$
1	−0·4°	−·40	1·99	−0·4°	−·201
2	−0·9	−·45	4·02	−0·9	−·223
4	−1·85	−·462	8·21	−1·85	−·225
6	−2·85	−·476	12·57	−2·85	−·226
8	−3·9	−·487	17·20	−3·9	−·226
10	−4·9	−·490	21·80	−4·9	−·224
14	−7·4	−·528	31·89	−7·4	−·232
18	−10·0	−·555	43·05	−10·0	−·231
					−·227

A constant quotient is found, however, in such cases if the salt is supposed to be in combination with water, and the percentage contents are calculated on this assumption; in the case of calcium chloride, it suffices to suppose that the solutions contain $CaCl_2.6H_2O$. To determine r, the number of molecules of water which must be taken as in combination with the salt, in such cases, it is necessary to find the contents of the solution in terms of this hydrate. If M is the weight of the anhydrous salt, with molecular weight A, then in place of M parts of the salt there must be taken in the calculation $M\left(1 + \frac{18}{A}r\right)$ parts (18 = molecular weight of water), and therefore there remain $100 - \frac{18}{A}r.M$, in place of 100 parts, of water; the quantity of the hydrate, S, in 100 parts of water is, therefore—

$$S = \frac{(A + 18r)\,M}{100\,A - 18rM}.100$$

In a second experiment, in a similar way,

$$S' = \frac{(A + 18r)\,M'}{100A - 18r\,M'} \cdot 100,$$

and as the law of proportionality shows that

$$S : S' = t : t'$$

it follows that

$$r = \frac{100\,A\,(Mt' - M't)}{18\,M.\,M'\,(t' - t)}.$$

Calculations made by this method lead to the supposition that the following hydrates exist in aqueous solutions :—

$CaCl_2.6H_2O$	−·227	$HCl.6H_2O$	−·251
$BaCl_2.2H_2O$	−·192	$HI.4H_2O$	−·157
$NaBr.4H_2O$	−·189	$H_2SO_4.9H_2O$	−·129
$NaI.4H_2O$	−·152	$HNO_3.4\frac{1}{2}H_2O$	−·230
$MnCl_2.12H_2O$	−·138	$NH_3.1\frac{1}{2}H_2O$	−·423
$CuCl_2.12H_2O$	−·127	$NaOH.1\frac{1}{2}H_2O$	−·509
$CuCl_2(NH_4Cl)_2.4H_2O$	−·373	$KOH.2H_2O$	−·394

The following seem to exist in solution as anhydrous salts :—

NH_4Cl	−·653	$NaNO_3$	−·370
$NaCl$	−·600	KNO_3	−·267
KCl	−·443	K_2CO_3	−·317
NH_4NO_3	−·384	$Ca(NO_3)_2$	−·277

The lowerings of the freezing-points are given for 1 per cent. of each salt in solution. Rüdorff lays especial weight on his experiments with common salt and copper chloride. The first appears as anhydrous in the above table. But it acts in this way only until the freezing-point is lowered to − 9°; the results after this are explained by supposing that the hydrate $NaCl.2H_2O$ is present. The following table illustrates the results :—

NaCl			
M	t	$\frac{t}{M}$	$\frac{t}{M_2}$
1	−0·6°	−·600	—
2	−1·2	−·600	—
4	−2·4	−·600	—
6	−3·6	−·600	—
8	−4·8	−·600	—
12	−7·2	−·600	—
14	−8·4	−·600	—
15	−9·2	−·613	−·340
16	−9·9	−·619	−·341
17	−10·6	−·623	−·341
18	−11·4	−·633	−·343
19	−12·1	−·637	−·342
20	−12·8	−·640	−·342

The numbers in the column headed $\frac{t}{M_2}$ are calculated on the assumption that the solution contains $NaCl.2H_2O$.

The change in the constitution of the solution is shown more forcibly by the results with copper chloride, where there is an accompanying colour-change. Dilute solutions are blue, and, according to Rüdorff, give quotients agreeing with the formula $CuCl_2.12H_2O$; more concentrated solutions are green, and give values pointing to the existence of the hydrate $CuCl_2.4H_2O$. M is referred to the anhydrous salt:—

M	t	$\frac{t}{M_4}$	$\frac{t}{M_{12}}$
2·39	−0·85°	−·229	−·125
4·91	−1·8	−·232	−·129
11·04	−4·6	−·257	−·131
14·94	−6·6	−·264	−·128
16·43	−7·4	−·267	−·127
16·53	−7·5	−·269	−·127
20·70	−10·0	−·280	−·124
22·45	−10·95	−·280	−·118
24·04	−12·05	−·284	−·118
25·46	−12·85	−·284	−·114
26·04	−13·1	−·282	−·110
28·46	−14·55	−·282	−·105
33·00	−17·4	−·282	−·055
33·88	−18·15	−·285	−·093

The numbers in the column for $CuCl_2 . 12H_2O$ are constant until 16 per cent. of $CuCl_2$ has been added; after that the numbers in the column for $CuCl_2 . 4H_2O$ are constant.

It may be remarked here that later investigations have brought to light much more complicated relations than Rüdorff supposed to exist. These investigations have shown, especially, that the change in the constitution of the solutions does not take place suddenly, but quite slowly, so that it is very doubtful whether the observations are to be interpreted as pointing to the existence of definite hydrates in solution.

3. **Experiments of Coppet.**—Ten years after the publication of Rüdorff's first paper, Coppet [1] took up the investigation and developed it in two directions. On the one hand, he made sure that the law of proportionality held good for supersaturated solutions also, and in this way he made it possible to obtain more accurate determinations for salts which had scarcely been examined before because of their small normal solubility in cold water. On the other hand, he referred the lowering of the freezing-temperature, not to equal quantities of salts, as Rüdorff had done, but to quantities which stood in molecular proportions. By doing this he arrived at a very simple expression for the influence of the salt on the freezing-point of the solution, as he found that the molecular lowerings of freezing-point were nearly equal for similar salts. Solutions whose contents were in the ratio of the molecular weights of the dissolved salts froze at nearly the same temperature.

I give the table in which Coppet combined the results of his own experiments with those of the experiments of Blagden and Rüdorff. The numbers in the column headed *h* represent depression-coefficients for 1 per cent. of salt, those under H represent the molecular depressions.

[1] *Ann. Chim. Phys.* (4) **23**, p. 366 [1871]; **25**, p. 502; **26**, p. 98 [1872].

	h	H		h	H
KCl	·451	33·6	$CaCl_2.15H_2O$*	·1135	43·2
KBr	·292	34·8	$CuCl_2.15H_2O$*	·127	44·5
KI	·212	35·2	$MnCl_2.15H_2O$*	·138	47·2
$NaCl.2H_2O$*	—	< 33·8	KNO_3	·267	27·0
$NaCl.3H_2O$*	—	> 31·4	$NaNO_3$	·310	26·4
$NaBr.3H_2O$	·216	33·9	$K_2CO_3.6H_2O$*	·161	39·6
$NaI.3H_2O$	·170	34·7	K_2CrO_4	·196	38·1
NH_4Cl	·650	34·8	K_2SO_4	·201 – ·244	35·0 – 39·0
$KOH.2H_2O$	—	< 33·9	$(NH_4)_2SO_4$	·276	36·4
$NaOH.1\frac{1}{2}H_2O$	—	< 34·1	$FeSO_4.7H_2O$	·055	15·3
NH_4OH*	·542	19·0	$ZnSO_4.7H_2O$	·055	15·8
$BaCl_2.15H_2O$*	—	> 43·4	$MgSO_4.7H_2O$	·073	18·0
$SrCl_2.15H_2O$*	—	> 41·6	$CuSO_4.5H_2O$	·070	17·5

The formulæ with an asterisk express hydrates which are not known in the solid state; the numbers preceded by > or < are calculated on certain assumptions which cannot be developed here.

The molecular depressions of the freezing-point are seen to be nearly equal in groups of similar compounds. They differ from group to group, but the numbers are of the same dimensions. It is noteworthy that the anhydrous salts give the same result as the salts with water of crystallisation; this is well seen in the haloid compounds of potassium and of sodium, e.g. KBr and $NaBr.3H_2O$.

Coppet devoted a great part of his labour to the study of the deviations from the law of proportionality which are exhibited by certain substances. The explanation which Rüdorff gave of those cases wherein the depression increased more rapidly than the contents of the solution has been noticed already; he supposed that water was combined chemically with the salt in solution. Coppet showed that Rüdorff's representation of the behaviour of common salt did not express the facts. Coppet's own experiments led to the result that the quotient began to increase, indicating a change of condition, even with the most dilute solutions, and not, as Rüdorff said, only when the temperature of about −9° was reached. In the other case carefully examined by Rüdorff, viz., that of copper chloride, the *very gradual*

change of colour from green to blue, which accompanies increasing dilution and falling temperature, indicates processes which are extended over a considerable space and do not take place suddenly.

Similar difficulties attend the explanation of the behaviour of those substances which lower the freezing-points of their solutions in a decreasing degree. Rüdorff gave no examples of this kind in his earlier communications, although he said afterwards[1] that such cases were known to him. Coppet was the first to make these cases known. Ammonium nitrate is a very striking example:

M	t	$\frac{t}{M}$	M	t	$\frac{t}{M}$
2	−0·83°	−·415	30	−9·35°	−·312
5	−2·03	−·406	40	−11·75	−·294
6	−2·40	−·400	50	−13·60	−·272
10	−3·85	−·385	60	−15·60	−·260
12	−4·55	−·379	70·24	−17·40	−·248
20	−6·90	−·345			

The nitrates of sodium, barium, calcium, strontium, and lead, and sulphate and carbonate of sodium, belong to the same class. Rüdorff adds also silver nitrate, ammonium sulphocyanide, and acetic acid.

Rüdorff did not publish his measurements of cases of this kind, because he could not suggest an explanation of them. Coppet, who had laïd down the theoretical possibility of occurrences similar to these in the case of the existence in the solution of several partially decomposed hydrates, supposed that the substances in question, many of which are certainly anhydrous, were 'modified,' in some way not more fully explained, by the action of the water or by the lowering of temperature. It will be shown afterwards that a modification of a peculiar kind, viz. electrolytic dissociation, gives an account of these facts.

The explanation which Lothar Meyer has given may,

[1] *Pogg.* **145**, p. 599 [1871].

perhaps, also be adopted, viz., that several molecules are gathered together into one in the more concentrated solutions—so that, e.g., molecules of the composition $(NH_4NO_3)_2$ may be present in a somewhat concentrated solution of ammonium nitrate—and that these gradually fall asunder as water is added. As the depression of freezing-point depends on the number of molecules in solution, but not on the number of atoms in these molecules, this depression must be less the greater the number of molecules which combine to form a single molecule.

The occurrence of cases of this kind throws great doubt on the calculations referred to on p. 201, which suppose the existence of hydrates in certain solutions. For as we cannot know, in these cases, whether the depression-coefficients of the salts themselves increase or decrease with increasing concentration, the foundation is removed on which the calculations were based, for that foundation was the supposition of an unchangeable coefficient.

4. **Investigations of Raoult.**—The problem of the molecular depression of the freezing-points of solutions has been very fully examined by Raoult within recent years. Raoult extended his investigations to other substances than salts. At the outset he subjected aqueous solutions of organic compounds to examination;[1] the result was that the molecular depressions of freezing-point were nearly the same for these compounds. The extreme values found were 15·5 and 22·9; or, rejecting these two, the extremes were 16·9 and 19·9. The molecular depressions of freezing-point were calculated for solutions of one-gram molecular weight of substance in 100 grams of water; the observations were generally made with solutions ten times more dilute, and containing, therefore, one gram-molecule per litre. In a second communication,[2] Raoult gave the results of similar experiments with solutions in very pure benzene, solidifying at 4·96°. Here, again, the depressions of freezing-point, calculated for quantities proportional to the molecular weights of the dissolved sub-

[1] *Compt. rend.* **94**, p. 1517 [1882]. [2] *Ibid.* **95**, p. 188 [1882].

stances, were found to be very nearly constant; they varied only from 48·6 to 51·8. Raoult obtained similar results with other solvents, viz., nitrobenzene, melting at 5·28°; ethylene dibromide, melting at 9·72°; formic acid, melting at 8·52°; and acetic acid, melting at 16·75°. He examined solutions of more than 200 different substances.[1] In the case of one series of substances, he found the molecular lowerings of freezing-point to be only half as great as the values obtained in most cases; the supposition at once suggests itself that the substances in question form double molecules in the solutions.

These simple relations were found to hold good not only for all solutions in one and the same solvent; Raoult also thought he found the same relations when he compared the constants for different solvents. The mean molecular depressions of freezing-point were—for solutions in water, 37 (or 18·5); in formic acid, 28; in acetic acid, 39; in benzene, 49; in nitrobenzene, 70·5; and in ethylene dibromide, 117. By dividing each of these numbers by the molecular weight of the solvent the following results are obtained:—

Water . . .	2·05 = 3 × ·683	Benzene	·628
Formic acid	·608	Nitrobenzene . . .	·600
Acetic acid	·650	Ethylene dibromide .	·623

These quotients are approximately constant. Raoult expressed the empirical results of his measurements in the following 'law':—'*One molecule of any compound, when dissolved in* 100 *molecules of a liquid, lowers the solidification-point of the liquid by an amount which is nearly constant*, viz. ·62°.' This statement involves the doubling, or trebling, of some of the molecular weights in common use; the molecular weight of water, for instance, must be multiplied by three. More recent work, which will be referred to later, has shown that such a general law as the above does not hold good.

The numbers which led Raoult to the foregoing

[1] *Compt. rend.* **95**, p. 1030.

statement were communicated by him in detail in 1884. The solutions used contained generally from $\frac{1}{2}$ to 1 gram molecular weight of the substance under examination in 1,000 grams of the solution; sometimes the solutions were even more dilute than this.[1]

The following table contains what Raoult calls the molecular depressions. If d be the lowering of freezing-point of a solvent caused by solution of p grams of a substance, having the molecular weight m, in 100 grams of the solvent, then $\frac{d}{p}$ is the *specific depression*, and $\frac{m\,d}{p}$ is the *molecular depression*. The molecular depression is, then, the lowering of the freezing-point which would be observed, assuming the law of proportionality, in a solution of one gram-molecular weight in 100 grams of the solvent.

Solutions in Acetic Acid.

	Mol. depression		Mol. depression
Methyl iodide	38·8	Butyric acid	37·3
Chloroform	38·6	Valeric „	39·2
Carbon tetrachloride	38·9	Benzoic „	43·0
Carbon disulphide	38·4	Camphoric acid	40·0
Hexane	40·1	Salicylic „	40·5
Ethylene chloride	40·0	Picric „	39·8
Turpentine oil	39·2	Water	33·0
Nitrobenzene	41·0	Methyl alcohol	35·7
Naphthalene	39·2	Ethyl „	36·4
Methyl nitrate	38·7	Butyl „	38·7
Methyl salicylate	39·1	Amyl „	39·4
Ether	39·4	Allyl „	39·1
Ethyl sulphide	38·5	Glycerin	36·2
Ethyl cyanide	37·6	Salicin	37·9
Ethyl formate	37·2	Santonin	38·1
Ethyl valerate	39·6	Phenol	36·2
Mustard oil	38·2	Pyrogallol	37·3
Aldehyde	38·4	Hydrocyanic acid	36·6
Chloral	39·2	Acetamide	36·1
Benzylic aldehyde	39·7	Ammonium acetate	35·0
Camphor	39·0	Aniline „	36·2
Acetone	38·1	Quinine „	41·0
Acetic anhydride	36·6	Strychnine „	41·6
Formic acid	36·5	Brucine „	40·0

[1] *Ann. Chim. Phys.* (6) **2**, p. 66.

Solutions in Acetic Acid—*continued.*

	Mol. depression		Mol. depression
Codeine acetate	38·3	Sulphuretted hydrogen	35·6
Morphine ,,	43·0	Sulphur dioxide	38·5
Potassium ,,	39·0		
Sulphur chloride	38·7	Sulphuric acid	18·6
Arsenious ,,	41·5	Hydrochloric acid	17·2
Stannic ,,	41·3	Magnesium acetate	18·2

Solutions in Formic Acid.

	Mol. depression		Mol. depression
Chloroform	26·5	Brucine formate	29·7
Benzene	29·4	Potassium ,,	28·9
Ether	28·2	Arsenious chloride	26·6
Aldehyde	26·1		
Acetone	27·8	Magnesium formate	13·9
Acetic acid	26·5		

Solutions in Benzene.

	Mol. depression		Mol. depression
Methyl iodide	50·4	Benzaldehyde	50·1
Chloroform	51·1	Camphor	51·4
Carbon tetrachloride	51·2	Acetone	49·3
Carbon disulphide	49·7	Valeran	51·0
Ethyl iodide	51·6	Acetic anhydride	47·0
Ethyl bromide	50·2	Santonin	50·2
Hexane	51·3	Picric acid	49·9
Ethylene chloride	48·6	Aniline	46·3
Turpentine oil	49·8	Narcotine	52·1
Nitrobenzene	48·0	Codeine	48·7
Naphthalene	50·0	Thebaine	48·0
Anthracene	51·2	Sulphur chloride	51·1
Methyl nitrate	49·3	Arsenious ,,	49·6
Methyl oxalate	49·2	Phosphorous chloride	47·2
Methyl salicylate	51·5	Phosphoric ,,	51·6
Ether	49·7	Stannic ,,	48·8
Ethyl sulphide	51·8		
Ethyl cyanide	51·6	Methyl alcohol	25·3
Ethyl formate	49·3	Ethyl ,,	28·2
Ethyl valerate	50·0	Butyl ,,	43·2
Mustard oil	51·4	Amyl ,,	39·7
Nitroglycerin	49·9	Phenol	32·4
Tri-butyrin	48·7	Formic acid	23·2
Tri-olein	49·8	Acetic ,,	25·3
Aldehyde	48·7	Valeric ,,	27·1
Chloral	50·3	Benzoic ,,	25·4

Solutions in Nitrobenzene.

	Mol. depression		Mol. depression
Chloroform	69·9	Codeine	73·5
Carbon disulphide	70·2	Arsenious chloride	67·5
Turpentine oil	69·8	Stannous „	71·4
Benzene	70·6		
Naphthalene	73·6		
Ether	67·4	Methyl alcohol	35·4
Ethyl valerate	73·2	Ethyl „	35·6
Ethyl acetate	72·3	Acetic acid	36·1
Benzaldehyde	70·3	Valeric „	42·4
Acetone	69·2	Benzoic „	37·7

Solutions in Ethylene Bromide.

	Mol. depression		Mol. depression
Carbon disulphide	117	Arsenious chloride	118
Chloroform	118		
Benzene	119	Acetic acid	58
Ether	117	Alcohol	57

Solutions in Water.[1]

	Mol. depression		Mol. depression
Methyl alcohol	17·3	Hydrocyanic acid	19·4
Ethyl „	17·3	Acetamide	17·8
Butyl „	17·2	Urea	17·2
Glycerin	17·1	Ammonia	19·9
Mannite	18·0	Ethylamine	18·5
Invert sugar	19·3	Propylamine	18·4
Milk „	18·1	Aniline	15·3
Cane „	18·5		
Salicin	17·2	Hydrochloric acid	39·1
Phenol	15·5	Hydrobromic „	39·6
Pyrogallol	16·3	Nitric „	35·8
Chloral hydrate	18·9	Perchloric „	38·7
Acetone	17·1	Arsenic „	42·6
Formic acid	19·3	Orthophosphoric acid	42·9
Acetic „	19·0	Sulphuric „	38·2
Butyric „	18·7	Selenious „	42·9
Oxalic „	22·9	Potash	35·3
Lactic „	19·2	Soda	36·2
Malic „	18·7	Lithia	37·4
Tartaric „	19·5	Potassium chloride	33·6
Citric „	19·3	Sodium „	35·1
Ether	16·6	Lithium „	36·8
Ethyl acetate	17·8	Ammonium „	34·8

[1] *Ann. Chim. Phys.* (5) **28**, p. 137 [1883].

SOLUTIONS IN WATER—*continued.*

	Mol. depression		Mol. depression
Potassium iodide	35·2	Sodium tartrate	44·2
Potassium bromide	35·1	Sodium di-tartrate	31·2
Potassium cyanide	32·2	Baryta	49·7
Potassium ferrocyanide	46·3	Strontia	48·2
Potassium ferricyanide	47·3	Lime	48·0
Sodium nitroprusside	46·8	Barium chloride	48·6
Potassium sulphocyanide	33·2	Strontium „	51·1
Potassium nitrate	30·8	Calcium „	49·9
Sodium „	34·0	Copper „	47·8
Ammonium „	32·	Barium nitrate	40·5
Potassium formate	35·2	Strontium „	41·2
Potassium acetate	34·5	Calcium „	37·4
Sodium „	32·0	Lead „	37·4
Potassium carbonate	41·8	Barium formate	48·2
Sodium „	40·3	Barium acetate	48·6
Potassium sulphate	39·0	Magnesium „	47·8
Potassium-hydrogen sulphate	34·8	Sulphurous acid	20·0
Sodium sulphate	35·4	Sulphuretted hydrogen	19·2
Ammonium „	37·0	Arsenious oxide	20·3
Borax	66·0	Metaphosphoric acid	21·7
Potassium chromate	38·1	Boric „	20·5
Potassium dichromate	43·7	Tartar emetic	18·4
Di-sodium phosphate	37·9	Mercuric cyanide	17·5
Sodium pyrophosphate	45·8	Magnesium sulphate	19·2
Potassium oxalate	46·8	Ferrous „	18·4
Sodium „	43·2	Zinc „	18·2
Potassium tartrate	36·3	Copper „	18·0

A glance through the series of numbers in the foregoing table shows that the molecular depressions of the freezing-point are generally nearly constant for solutions in one and the same solvent. But besides the *normal* values, which are found for by far the greater number of substances, there are *abnormal* values belonging to a small number of substances. Omitting the salts and the mineral acids, which must be dealt with separately, all the values obtained for solutions in acetic acid and formic acid are normal. Solutions of the alcohols and acids in benzene show abnormal values, and these values are generally half as large as those of the other substances. The same compounds show quite similar deviations when dissolved in nitrobenzene and in ethylene

bromide. The supposition is at once suggested that the compounds in question have molecular weights in these solutions twice as great as those usually adopted for these compounds. The circumstance that the molecular weights of the fatty acids in the gaseous state are greater than the formulæ of these acids indicate, and that normal values are attained only at temperatures considerably above the boiling-points of the acids, is in favour of this supposition. The alcohols, it is true, do not behave in this way; but the phenomena of surface-tension make it probable that the liquid alcohols consist of polymeric molecules.[1]

We may then conclude that the action of acetic and formic acids as solvents is unfavourable to the existence of polymeric molecules, just as the action of a high temperature or a small pressure is unfavourable to the existence of such molecules; but that benzene, nitrobenzene, and ethylene bromide act in an opposite way, and do not promote the falling asunder of the more complex into the less complex molecules. This way of viewing the subject is made more probable by the fact that the *same* substances form double molecules in all three solvents.

5. **Aqueous solutions.**—Different conditions prevail in aqueous solutions. All the organic compounds examined show agreement when dissolved in water; neither alcohols nor fatty acids show any tendency to cause molecular depressions of half the normal value. We may conclude, therefore, that water, like acetic acid, acts against the formation of polymeric molecules.

But, in contradistinction to the other solvents, water shows not too small, but too great, molecular depressions, when it is used as a solvent for the acids, bases, and salts, that is, for electrolytes. The molecular depressions caused by strong monobasic acids, monoacid bases, and salts of the type of potassium chloride, are almost twice as great as those caused by indifferent substances; and the values

[1] These phenomena are considered in an earlier part of the *Lehrbuch*.—*Translator*.

become almost three times the ordinary values in the cases of the hydroxides and haloid compounds of the divalent earth metals. Such more complex salts as borax, ferrocyanide of potassium, &c., give yet larger values.

The supposition which was made use of in dealing with the other solvents cannot find acceptance here. The converse conception must rather be adopted. *We must regard the substances which give abnormally large molecular depressions as dissociated.*

This supposition receives considerable support from the conclusions arrived at by Arrhenius,[1] and simultaneously by Planck,[2] by comparing the depressions of freezing-point with the lowerings of vapour-pressure. In each case the molecular weight of the dissolved substance may be determined, in reference to that of the solvent, by the formula $\frac{p - p'}{p} = \frac{n}{N}$; the organic compounds were generally found to be normal, but aqueous solutions of electrolytes showed a greater number of molecules than the formula required, and consequently it was necessary to assume that a separation of molecules had occurred. The method based on measurements of the lowerings of freezing-point does not appear to furnish an immediate criterion of the kind required. We shall see later, however, that van't Hoff has arrived at a formula, from considerations similar to those made use of for vapour-pressure, which makes possible the immediate estimation of molecular weights. Meanwhile it is clear that a comprehensive survey of the observations renders the supposition untenable that all indifferent substances are polymerised, and that the values found for salts are the normal values. This is shown at once by the fact that the molecular depression caused by the salts themselves is by no means constant, but varies with the nature of the salt. If potassium chloride, and salts

[1] *Zeitschr. f. physikal. Chemie*, 1, p. 631 [1887]; from *Ofv. Stockh. Akad.* June 8 and November 9, 1887.

[2] *Ibid.* 1, p. 576 [1887].

similar to this, for instance, are taken as normal, then it is necessary to suppose that barium chloride, &c., have undergone separation, inasmuch as they show a greater molecular depression. Raoult's numbers show that this supposition is to be avoided only by taking as normal the salt with the greatest molecular depression, i.e. borax: but the choice of this salt as the normal substance could scarcely be expected to be generally accepted.

Raoult thought he could place the behaviour of water as a solvent parallel with that of the other solvents;[1] but at that time he did not know the relations between the facts and those of vapour-pressures, which do so much to make the subject clear, and which he himself at a later time has greatly advanced. In a communication made soon after that just referred to, Raoult[2] developed a way of regarding the subject which differed from his former method. Following the announcement of de Vries, that the metals and acidic radicles may be grouped in accordance with their valencies, Raoult sought to express the freezing-points of solutions as approximately the sums of two constants, one of which belonged to the metal and the other to the acidic radicle. I do not go into this subject here, inasmuch as Raoult's expression has been replaced by one put forward by Arrhenius, which is much more comprehensive and more convenient, and which will be considered in its proper place.

6. **Use of the law of solidification for determining molecular weights.**—The simple relations between the molecular weight and the depression of freezing-point afford a very convenient means for determining the molecular weights of dissolved substances. Raoult, especially, has made reference to this subject; he has given the following rules of procedure. The molecular weight, m, of any organic substance is given by the formula

$$m = \frac{K}{A},$$

[1] *Ann. Chim. Phys.* (6) **2**. p. 85 [1884]. [2] *Ibid.* (6) **4**, p. 401 [1885].

where A is the specific depression of freezing-point, i.e. the quotient obtained by dividing the observed depression by the percentage contents of the solution, and K is a constant dependent on the nature of the solvent. The values of this constant are

Water	K = 19
Acetic acid	K = 39
Benzene	K = 49

If different (multiple) values are obtained for solutions in different solvents, the smaller value is the more accurate. The molecular weights of certain inorganic chlorides, e.g. $AlCl_3$, PCl_3, &c., may be determined, similarly to organic compounds, from the freezing-points of their solutions in acetic acid or benzene.

In dealing with salts it is necessary to distinguish two cases, according as the basicity of the acid or the valency of the metal is to be determined. In the first case, the sodium or potassium salt is to be used, and the observed depression of freezing-point is to be referred to one atom of the metal; i.e. the equivalent, and not the molecular, depression is to be found. If the value is about 35, the acid is monobasic; if 20, the acid is dibasic; and if about 15, it is tri- or tetra-basic. If it is desired to find the valency of the metal, the nitrate should be used, and the equivalent depression of freezing-point is to be determined. If the number which is found is about 35, the metal is monovalent; a divalent metal gives about 22·5, and if the number is still smaller the metal is polyvalent.

One might well suppose that a process which enriches chemical method by extending the determination of molecular weights from the comparatively narrow field of gasifiable and vaporisable substances to the much ampler domain of solutions, would have been received with enthusiasm and put into practice with eagerness. But it must

be admitted that nothing of the kind occurred. Notwithstanding their significance, Raoult's results remained, at first, unnoticed; and the demonstration of the practical importance of these results which was given in the first edition of this *Lehrbuch*, published in 1885, did not effect any immediate change. In 1886, it is true, Paterno and Nasini [1] repeated some of Raoult's experiments, and instituted some new ones with various substances, especially with polymerides, which for the most part confirmed the laws arrived at by Raoult. In spite of the great service which these results seemed likely to render to organic chemistry, two years elapsed before the method began to come into general use.

The theoretical considerations which van 't Hoff put forward regarding the nature of solutions had a decided effect in increasing the interest in the phenomena examined by Raoult. There was a certain hesitation in dragging into chemical disputes the regularities which Raoult had arrived at by observation, because, although they had been verified sufficiently, they were yet purely empirical statements; but when these statements were shown to be necessary consequences from more general laws, it was felt that they might be used with greater security.

7. **Comparison of the lowerings of freezing-points and vapour-pressures.**—The close relation between the change of vapour-pressure and the change of freezing-point following the addition of a salt to water, which makes itself apparent in the corresponding forms of the laws, suggests a connexion between the numerical values of both effects. Such a connexion has been established by Raoult [2] in a purely empirical way. He examined 18 salts with respect to both properties; the depressions of vapour-pressure refer to 100°; they were determined partly by the barometric, and partly by the boiling-point, method.

[1] *Lincei*, **3** [1886]; *Berichte*, **19**, p. 2522.
[2] *Compt. rend.* **87**, p. 167 [1878].

Salts	Freezing-point	Vapour-pressure	
Mercuric chloride . . .	·048	·058 × 7·6	15·7
Mercuric cyanide . . .	·059	·087 × 7·6	21·9
Lead nitrate	·104	·110 × 7·6	36·3
Barium ,, ...	·145	·137 × 7·6	35·6
Silver ,, ...	·145	·160 × 7·6	27·2
Potassium ferricyanide . .	·146	·165 × 7·6	54·3
Potassium chromate . .	·200	·213 × 7·6	41·3
Potassium sulphate . .	·210	·201 × 7·6	35·0
Potassium iodide . . .	·215	·225 × 7·6	37·3
Potassium chlorate . .	·215	·240 × 7·6	29·4
Potassium nitrate . . .	·245	·280 × 7·6	28·3
Ammonium sulphate . .	·273	·230 × 7·6	28·1
Potassium bromide . .	·295	·310 × 7·6	36·9
Sodium nitrate . . .	·347	·380 × 7·6	32·3
Ammonium ,, . . .	·378	·361 × 7·6	32·5
Potassium chloride . .	·446	·450 × 7·6	33·5
Sodium ,, . .	·660	·604 × 7·6	35·3
Ammonium ,, . .	·639	·565 × 7·6	30·2

This tabulation of the results shows that the salts stand in nearly the same order as regards their influence both on the freezing-point and on the boiling-point; to make the comparison more evident, the numbers in the second series are divided by 7·6, which is the mean value of the ratio. I have added in each case the products obtained by multiplying the observed numbers by this mean ratio. Speaking generally, the effect of the salt increases in proportion as the atomic weight decreases.

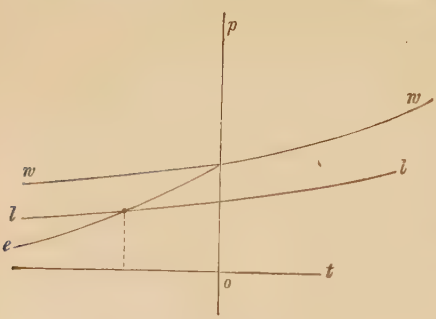


Fig. 26

The relation thus established empirically by Raoult had been deduced theoretically, some years before, by Guldberg.[1] Inasmuch as salt-solution and ice exist together at the freezing temperature of a salt-solution, it may be shown [2]

[1] *Compt. rend.* **70**, p. 1349 [1870].

[2] The method of proof is elucidated in an earlier chapter.—*Translator.*

that the vapour-pressure must be the same over ice as over the solution at the freezing temperature, as otherwise a perpetual motion would be possible. In a system of co-ordinates, the abscissæ of which represent temperatures and the ordinates represent vapour-pressures (fig. 26), let w be the pressure-curve of water, and e that of ice (which Kirchoff has shown to agree with that of water with a break at 0°), and let l be that of the solution; then the freezing-point of the solution is determined by the abscissa of the point of intersection of e and l. Now, by the law of Babo and Wüllner (p. 157) the proportional decrease of the vapour-pressure of the solution, p, compared with that of water, p_0, is expressed by the formula $\frac{p_0 - p}{p_0} = a c$, where c is the concentration, i.e. the quantity of salt divided by the quantity of water, and a is a constant.

Another expression may be found for the magnitudes of the pressures. According to the dynamical theory of heat, the relation between the quantity of heat, r_0, required to evaporate unit weight of liquid, which in this case is water, the pressure, and the volume of the saturated vapour, v, is expressed thus :—[1]

$$\frac{r_0}{\text{A T}} = \frac{d p_0}{d \text{T}} . v,$$

where T is the absolute temperature, and $\frac{1}{\text{A}}$ is the mechanical equivalent of heat. By substituting for v from the equation $p_0 v = \text{R T}$, it follows that

$$\frac{r_0}{\text{A R T}^2} = \frac{d}{dt} \log. p_0.$$

A similar formula holds good for ice, only the heat of vaporisation, r_1, is greater, as the heat of fusion must be added; we have

$$\frac{r_1}{\text{A R T}^2} = \frac{d}{dt} \log. p_1,$$

[1] Strictly speaking, v should be diminished by the volume of the water.

where p_1 is the vapour-pressure of ice; the difference between these two is

$$\frac{r_1 - r_0}{\text{ART}^2} = \frac{d}{dt}\left(\log.\frac{p_1}{p_0}\right).$$

Now, as was seen above, $r_1 - r_0$ is the heat of fusion of ice, r, and this has the value, $r = 79{\cdot}04 + {\cdot}49\,t$. Substituting, we obtain

$$d \log.\frac{p_1}{p_0} = \frac{79{\cdot}04 + {\cdot}49\,t}{\text{ART}^2}\,dt.$$

The integral gives approximately $\log.\frac{p_1}{p_0} = {\cdot}00954\,t$ for the vapour-curve of ice. Now it was found above that $\frac{p_0 - p_1}{p_0} = a\,c$, therefore $\frac{p_1}{p_0} = 1 - a\,c$, and we have

$$\log.\frac{p_1}{p_0} = {\cdot}00954\,t = \log.\,(1 - a\,c).$$

By developing the logarithm, and neglecting the terms from the second onwards, it follows that ${\cdot}00954\,t = -\,a\,c$, or

$$t = -\,105\,a\,c.$$

By combining the equation for the vapour-curve of ice with that for the salt-solution, with elimination of the equal pressure, the point of intersection of both curves is found, and we thus obtain the relation between the change of vapour-pressure and the change of freezing-point caused by the salt. This turns out to be nothing else than the law of Blagden; the freezing-point, $-t$, changes in proportion with the salt-contents, c. If the constant a, the proportional lowering of vapour-pressure by the unit quantity of salt, is calculated from the experiments of Wüllner, and the corresponding values are put in the equation $t = -\,105\,a\,c$, the lowerings of freezing-point are obtained. The results of this calculation are given in the annexed table, c being taken as $\frac{1}{100}$. Considering the

approximate character of the calculation, and the differences of kind between the numbers, the agreement may be regarded as sufficiently close.

	Wüllner	Rüdorff
NaCl	·601	·600
KCl	·390	·443
Na_2SO_4	·236	·297
K_2SO_4	·383	·201
$NaNO_3$	·315	·370
KNO_3	·196	·267
$CaCl_2.5H_2O$	·247	·227
$KOH.2H_2O$	·332	·395
$NaOH.1\frac{1}{2}H_2O$	·409	·509

8. **Theory of van 't Hoff.**—From the foregoing demonstration given by Guldberg, that the depression of the freezing-point and that of the vapour-pressure must be proportional, and from the proportionality which has been shown (p. 184) to exist between the latter and osmotic pressure, the existence of a corresponding connexion between osmotic phenomena and those shown in the freezing of solutions follows necessarily. This connexion was first made known by van 't Hoff, who has made use of it to deduce the laws of the lowering of the freezing-points of solutions in a more general form than Guldberg could give to them twenty years ago. The following exposition repeats, in slightly altered form, the reasoning used by van 't Hoff.

Let there be a large quantity of a solution consisting of n molecules of the dissolved substance, and N molecules of the solvent. Let T be the freezing-temperature of the pure solvent. We lower this temperature to $T - \Delta$ till the solvent separates in the solid form, and we allow as much to solidify as served to dissolve one molecule of the substance, that is $\frac{N}{n}$ molecules—the quantity corresponding with the molecular weight, taken in grams, being always reckoned as a molecule. The heat thus produced is an infinitely small quantity of the first order, $\frac{N}{n}\lambda$, where λ is the molecular

heat of fusion of the solvent. We now separate the ice and the solution and warm both to the original temperature T; by this process the ice is melted, and the quantity of heat, $\frac{N}{n}\lambda$, is again used. Finally we allow the quantity of pure solvent thus obtained to mix with the solution through a semi-permeable partition. If p is the osmotic pressure of the solution, we gain the work $p\,v$, where v is the volume of the solvent which was present as ice.

According to a statement already made use of, the relation which the amount of work to be gained bears to the total quantity of heat added, in a reversible cyclical process, is equal to that of the temperature-difference to the absolute temperature of the change. The work is $p\,v$, the total quantity of heat is $\frac{N}{n}\lambda$; we have then,

$$\frac{p\,v\,n}{N\lambda} = \frac{\Delta}{T}.$$

Now $p\,v = R\,T$; the constant R has the ordinary value, viz. 2 cals. in thermal measure. As we are dealing here, as elsewhere, with one gram-molecule of the dissolved substance, it follows, therefore, that

$$2\frac{T\,n}{N\lambda} = \frac{\Delta}{T} \text{ or } \Delta = \frac{n}{N} \cdot \frac{2\,T^2}{\lambda}.$$

The depression of the freezing-point, Δ, caused by the dissolved substance is proportional to the number of molecules of this substance in a specified number, N, of molecules of the solvent, and farther, it is proportional to the quantity $\frac{2\,T^2}{\lambda}$, which is dependent only on the nature of the solvent.

Comparing this result with the empirical law of Raoult, given by him in the form (p. 215)

$$m = \frac{K}{A},$$

it becomes possible to calculate the constant, K, as follows.

The specific depression, A, is equal to $\frac{\Delta}{p}$, where p is the percentage contents of the solution, and Δ is the corresponding depression of the freezing-point. The number of molecules of the dissolved substance, n, in 100 grams of the solvent is therefore $n = \frac{p}{m}$, and the number of molecules of the solvent is $N = \frac{100}{M}$, where m and M are the molecular weights of the dissolved substance and the solvent, respectively. By substituting the first values in Raoult's equation we have,

$$\Delta = K n;$$

and substituting $N = \frac{100}{M}$ in van 't Hoff's equation we obtain,

$$\Delta = \frac{n M}{100} \cdot \frac{2 T^2}{\lambda};$$

and from both of these,

$$K = \frac{M}{100} \cdot \frac{2 T^2}{\lambda} = \frac{2 T^2}{100 L},$$

if we put $\lambda = L M$, where L is the ordinary heat of fusion calculated for 1 gram of the substance.

It is possible then to calculate the constant K, found empirically by Raoult, from the heat of fusion, L, and the melting-point. Van 't Hoff has carried out this calculation with the following results:—

	T	L	$\frac{2T^2}{100L}$	K
Water	273°	79	18·9	18·5
Acetic acid . . .	290	43·2	38·8	38·6
Formic acid . . .	281·5	55·6	28·4	27·7
Benzene . . .	277·9	29·1	53·0	50·0
Nitrobenzene . . .	278·3	22·3	69·5	70·7

Considering the difficulties and uncertainties which

attend determinations of heats of fusion, the agreement between the figures in the fourth and fifth columns may well be regarded as a remarkable confirmation of the theory of van 't Hoff. The heat of fusion of nitrobenzene was not known before the publication of van 't Hoff's memoir; he calculated it to be 22·1 cals., using the constant found by Raoult; and Petterson, who made a direct determination at the request of van 't Hoff, found the heat of fusion to be 22·3 cals.

The testing of the foregoing formula has been carried farther. The formula is not in keeping with the statement made by Raoult, that one molecule of a substance dissolved in 100 molecules of a solvent bring about a depression of the freezing-point the mean value of which is ·62°. This statement is represented by the equation

$$\frac{n}{N} = \frac{\Delta}{\cdot 62 \times 100}$$

where the letters have the same significance as before. But the equation of van 't Hoff reads,

$$\frac{n}{N} = \frac{\Delta \lambda}{2T^2};$$

hence, if both equations are right, it follows that

$$\lambda = \frac{2\,T^2}{62} = \frac{T^2}{31}.$$

The molecular heat of fusion must then be proportional to the square of the fusion-temperature.

Eykman [1] has examined the depressions of the freezing-points of several solvents produced by dissolving in them substances of known molecular weights. The following table exhibits the results of comparing the observed molecular depressions with those calculated by the formula of van 't Hoff, on the one hand, and those calculated by Raoult's rule, on the other hand:—

[1] *Zeitschr. f. physikal. Chemie*, 3, p. 203 [1889].

	Observed	According to van 't Hoff	According to Raoult
Phenol	74	77	58·3
Naphthalene	69	69·4	79·4
p-Toluidine	51	49	66·3
Diphenylamine	88	98·6	104·8
Naphthylamine	78	102·5	88·7
Lauric acid	44	45·2	124
Palmitic acid	44	(about) 44·3	158·7

Van 't Hoff's formula gives decidedly better results than Raoult's rule for phenol, naphthalene, and toluidine; both formulæ show considerable, and about equal, deviations from the numbers observed for diphenylamine and naphthylamine; the numbers calculated by van 't Hoff's formula for lauric and palmitic acids are almost identical with the observed numbers, whereas Raoult's rule leads to numbers which are three to four times too large. The reason for the discrepancies between the observed and calculated numbers for diphenylamine and naphthylamine probably lies in the uncertainty of the values found for the heats of fusion of these compounds; the melting-points of the specimens used by Batelli did not point to the complete absence of impurities. If the heats of fusion, L, are calculated, by the formula of van 't Hoff, from the observed molecular depressions of freezing-point, the results are as follows:—

	Observed	Calculated
Phenol	25	26·1
Naphthalene	35·5	35·7
p-Toluidine	39	38·6
Diphenylamine	21·3	24·4
Naphthylamine	19·7	26·4
Lauric acid	43·7	44·9
Palmitic acid	50 (?)	50·4

The number for palmitic acid was not observed directly, but it was calculated from the values for lauric and myristic acids. More recently, Eykman[1] has tested

[1] *Zeitschr. f. physikal. Chemie*, **4**, p. 517 [1889].

and confirmed the formula of van 't Hoff by direct and indirect estimations of some heats of fusion. The numbers are :—

	Direct observation	Calculated by van 't Hoff's formula
Thymol	27·5	27·9
Diphenyl	28·5	29·4
Azobenzene	29	29·4
Urethane	40·8	41

The agreement is satisfactory in every case.

9. **Practical application of the method.**—The law of the depression of the freezing-point began to be more used in the solution of special chemical problems about the year 1888. I was able to show, by the application of this law, that an aqueous solution of chromium trioxide contains dichromic acid, $H_2Cr_2O_7$, and not chromic acid, H_2CrO_4, as was generally supposed.[1] Soon after this V. Meyers and Auwers[2] pointed out the usefulness of the freezing-method in a special case, and Auwers described a method of procedure. Methods were also described by Hollemann,[3] Hentschel,[4] and Beckmann.[5] The last-named took up the problem very zealously, and to him we owe both a practical arrangement, which is now pretty widely used, and also a large number of accurate determinations.

The apparatus used by Beckmann[6] is represented in fig. 27. It consists of a vessel, A, the size of a large test-tube, furnished with a side-tube; this is placed in the wider but shorter tube, B, which serves as an air-jacket. Both vessels pass through the lid of a stout cylindrical glass, C, in which the cooling material is placed. The tube A is closed with a cork which carries a thermometer, and also a piece of stout platinum wire bent at the end to form a stirrer. The

[1] *Zeitschr. f. physikal. Chemie*, **2**, p. 78 [1888].
[2] *Berichte*, **21**, pp. 536, 701 [1888].
[3] *Ibid.* **21**, p. 860.
[4] *Zeitschr. f. physikal. Chemie*, **2**, p. 306.
[5] *Ibid.* **2**, p. 638 [1888].
[6] Beckmann has recently described certain changes and improvements (see *Zeitschr. f. physikal. Chemie*, **7**, p. 323 [1891]).

thermometer must be very delicate—it is advantageous to divide it into hundredths of a degree—but the readings need only extend over a small range, 5° to 10° being sufficient. To make the thermometer applicable for different solvents, the upper end of it is attached to the contrivance shown in fig. 28, which is an improvement on a device introduced by Walferdin. The capillary tube of the thermometer is bent, and then widened into a little vessel, which ends in a capillary tube opening upwards for the purpose of more easily filling the thermometer. The instrument contains

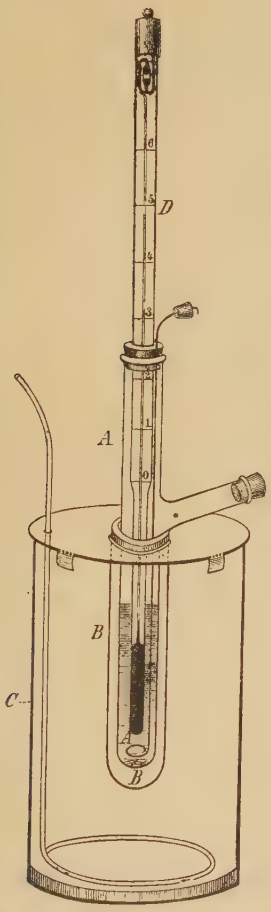


Fig. 27

Fig. 28

enough mercury to allow readings to be taken at the lowest temperatures likely to be found in the experiments. To make the thermometer available for some solvent, e.g. for acetic acid, it is warmed slightly above the melting-point of the solvent, and then shaken with a short perpendicular motion.

The mercury in the small vessel at the top of the thermometer is thus separated at the part where the little vessel becomes capillary, and the mercury-thread passes into the graduated part of the tube when the thermometer is cooled. If too much mercury has been cut off, the thread is caused to enter the little vessel by warming, the mercury in the vessel is joined to the thread by a swinging motion, and the mercury is again separated when the required temperature has been carefully established.

An experiment is conducted as follows. The vessel A is weighed, and about 25 grams of the solvent, weighed to within ·01 gram, are placed in it. The pieces of the apparatus are then put together; the outer vessel contains cold water if acetic acid is the solvent used, ice and water if benzene is used, and ice and common salt if water is the solvent employed. The solvent is allowed to freeze, while the stirrer is kept in constant motion, and the freezing-point is noted. The substance under examination is now added, through the side-piece, from a convenient weighing-vessel, which is then again weighed, and the weight of the substance added is thus determined. As the temperature at which the solution and ice are in equilibrium is dependent, for one and the same solution, on the quantity of the latter, it follows that this quantity should be made as small as possible. In order to get an accurate measurement, it is advisable to overcool the solution somewhat at first, and then to cause the ice to form by careful stirring. For this purpose, the vessel A is at once plunged into the cooling material without the mantle B, and some ice is thus formed; this ice is then allowed to melt until only a little of it remains, and then A is surrounded by the mantle B, and placed in the cooling material. As soon as the temperature has sunk a few tenths of a degree below the freezing-point (which is supposed to be known approximately), the stirrer is set into vigorous motion, and the separation of finely divided ice soon begins. The thermometer rises for a few moments, it then remains stationary for a longer time, and

then, as greater quantities of ice separate, it sinks slowly. The highest temperature observed is the correct temperature of freezing.

A second portion of the substance under examination should be added to the solution, immediately the first experiment is finished, and a new determination should be made to control the first.

The molecular weight is calculated by Raoult's formula (p. 215)

$$m = \frac{K}{A}.$$

That the observed number may be directly put into this equation, we must pay attention to the fact that A is the lowering of the freezing-point caused by 1 per cent. of the dissolved substance. If we have used G grams of the solvent, and g grams of the dissolved substance, and have observed the lowering of the freezing-point of the solvent to be Δ, then $A = \frac{\Delta\ G}{100\,g}$, and hence

$$m = 100\ K \frac{g}{\Delta\ G}.$$

The values of K are,

	Raoult's mean value	Calculated from heat of fusion
Water	18·5	18·9
Acetic acid	38·6	38·8
Benzene	50·0	53·0

The numbers in the second column are to be preferred to those in the first, inasmuch as the heats of fusion of the three solvents are known very accurately.

Other pieces of apparatus have been described. Klobukoff devised an arrangement which is convenient to work with, and gives accurate results, but the construction is rather complicated.[1] The arrangement proposed by Eykman [2] is very simple. It consists of a small flask with

[1] *Zeitschr. f. physikal. Chemie*, **4**, p. 10 [1889]. [2] *Ibid.* **2**, p. 964 [1888].

a thermometer ground into the neck, and placed in an ordinary glass cylinder (fig. 29). There is a contrivance, similar to that used by Beckmann, at the top of the thermometer, to make it suitable for different regions of temperature. Eykman contents himself with a division into tenths of a degree, as the freezing-temperature remains constant sufficiently long to enable hundredths of a degree to be estimated by the help of a telescope. This apparatus is especially applicable for solvents which melt above the ordinary temperature of the laboratory, e.g. for phenol and similar solvents.

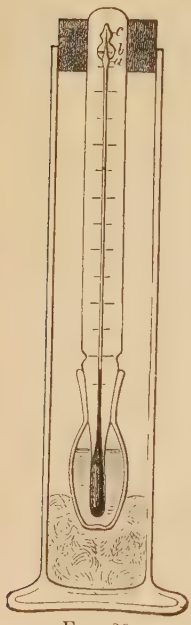


Fig. 29

Finally, it should be mentioned that R. Fabinyi [1] used naphthalene as a solvent; he rubbed the (solid) substance to be examined with the proper quantity of naphthalene to fine powder in a mortar, and then determined the melting-point of the mixture, in the ordinary way, by placing a little of the mixture in a small capillary tube, strapping this to a thermometer, and warming slowly. The results of this process served only as first approximations; Fabinyi, therefore, at a later time, preferred to heat slowly larger quantities of the mixture in a test tube, with an immersed thermometer and a stirrer, and thus to determine the temperature of melting. The process is limited to solvents which, like naphthalene, do not take up moisture from the air, as the presence of moisture often affects melting-points to a considerable extent.

10. **Solidification-points of alloys of metals.**—The general laws regarding freezing-points, like those regarding vapour-pressures, have been found to hold good for solutions of metals in metals. Tammann [2] examined solutions of metals

[1] *Zeitschr. f. physikal. Chemie*, 3, p. 38 [1889].
[2] *Ibid.* 3, p. 441 [1890].

in mercury, and also in sodium, and obtained the following numbers:—

SOLUTIONS IN MERCURY; K = 425.

	Molecular weight calculated	Atomic weight
Potassium	25·8–55·2	39·1
Sodium	20·6–24·9	23·0
Thallium	141–221	204·1
Zinc	52–66	65·5

These metals seem to be separated into monatomic molecules. The value which was used for K was calculated from the heat of fusion by van 't Hoff's formula. The solutions in sodium gave results for which no simple explanation could be found.

These phenomena have been examined more fully by Heycock and Neville.[1] In their first communication they used sodium as a solvent, and they found the following depressions caused by solution of one atom of the specified metal in 100 atoms of sodium:—

	Atomic depression
Gold	4·87–4·50
Thallium	4·27–4·73
Mercury	4·37–4·53
Cadmium	3·17–3·92
Potassium	3·34–3·85
Indium	3·37–3·77

In their second communication tin was used as the solvent. The observed atomic depressions were as follows for solutions of small concentrations:—

	Atomic depression		Atomic depression
Nickel	2·94	Lead	2·76
Silver	2·93	Tin	2·64
Gold	2·93	Cadmium	2·43
Copper	2·91	Mercury	2·39
Thallium	2·86	Bismuth	2·40
Sodium	2·84	Calcium	2·40
Palladium	2·78	Indium	1·86
Magnesium	2·76	Aluminium	1·25

[1] *Chem. Soc. Journal*, Trans. 1889, p. 666; 1890, p. 376.

These solutions evidently obey the law of Coppet and Raoult. Indium, and especially aluminium, show a depression which is too small, and, therefore, these metals exhibit a tendency to form complex molecules.

11. **Influence of concentration.**—An account has been given of the observations which show that solutions of many salts do not obey Blagden's law of proportionality. The depression-coefficients of some substances decrease, and those of other substances increase, as concentration increases.

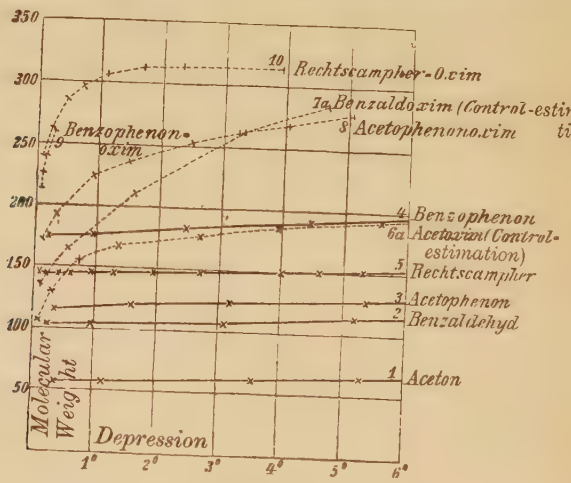


FIG. 30

Similar phenomena are noticed with solutions of indifferent substances, and when different solvents are used. Raoult subjected such cases to a fairly thoroughgoing investigation,[1] which, however, applied almost wholly to solutions of salts, whose special behaviour will not be discussed by us at present.

The first thorough examination of the effect of concentration on the freezing-points of solutions of indifferent substances was made by E. Beckmann,[2] with the following results. In by far the greater number of cases, the molecular weight calculated by the formula changes nearly in

[1] *Ann. Chim. Phys.* (6) **8**, p. 289 [1886].
[2] *Zeitschr. f. physikal. Chemie*, **2**, p. 715 [1888].

proportion to the concentration, and it generally increases, but occasionally it decreases, as the concentration increases. If the relation is represented graphically, using the concentrations—or the freezing-points which are nearly proportional to the concentrations—as abscissæ, and the calculated

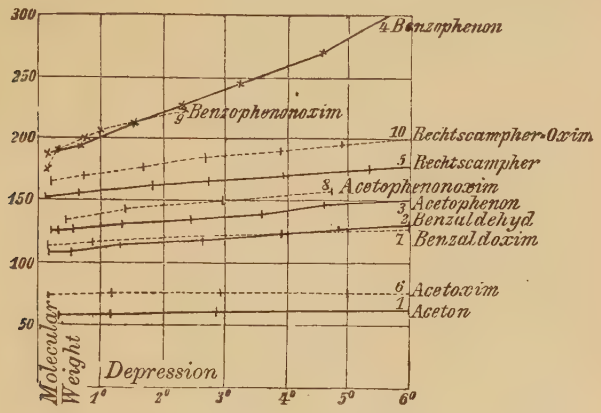


FIG. 31

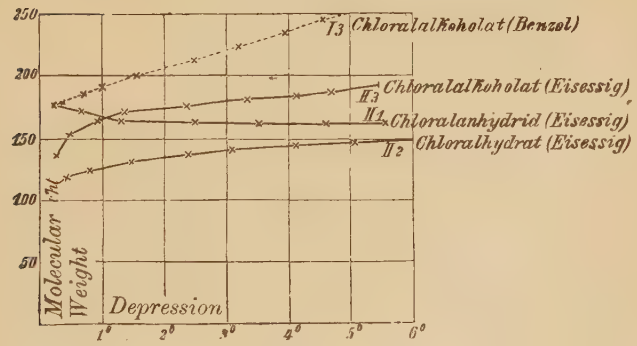


FIG. 32

molecular weights as ordinates, the curves run almost straight, with a slight inclination towards the axis of the abscissæ. Figures 30 to 34 show the relations in question very clearly.[1]

[1] As these plates are printed from the German electrotypes, the German names for the various compounds are retained; these names are so nearly

The behaviour of some of the compounds represented in fig. 30 differs considerably from that of most of the other substances; these abnormal compounds are dextro-camphor-oxim, benzaldoxim, acetophenoxim, and acetoxim. The

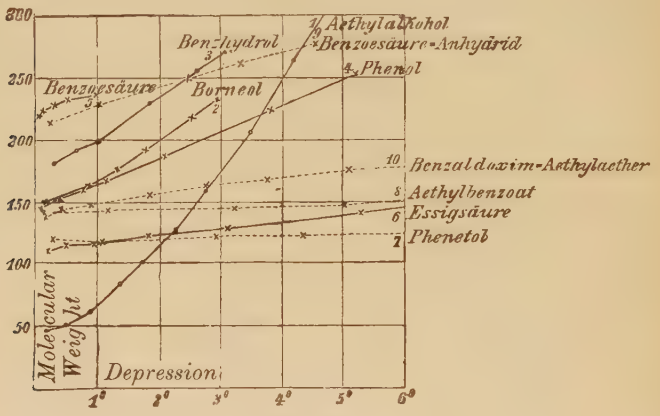


Fig. 33

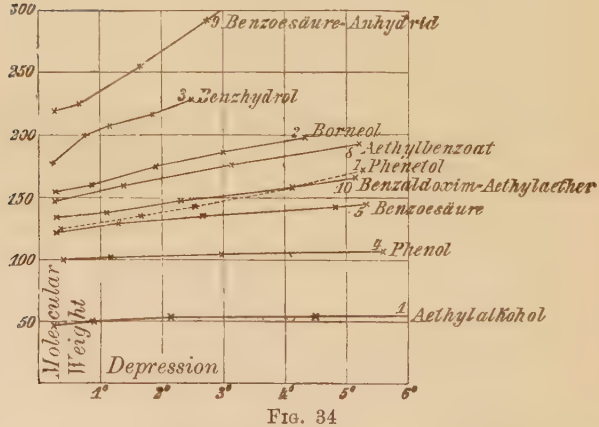


Fig. 34

curves of these compounds show a marked curvature, in place of being nearly straight lines, and indicate an increase of the molecular weights to nearly double the original

the same as the English names that English students will find no difficulty in translating them.—*Translator.*

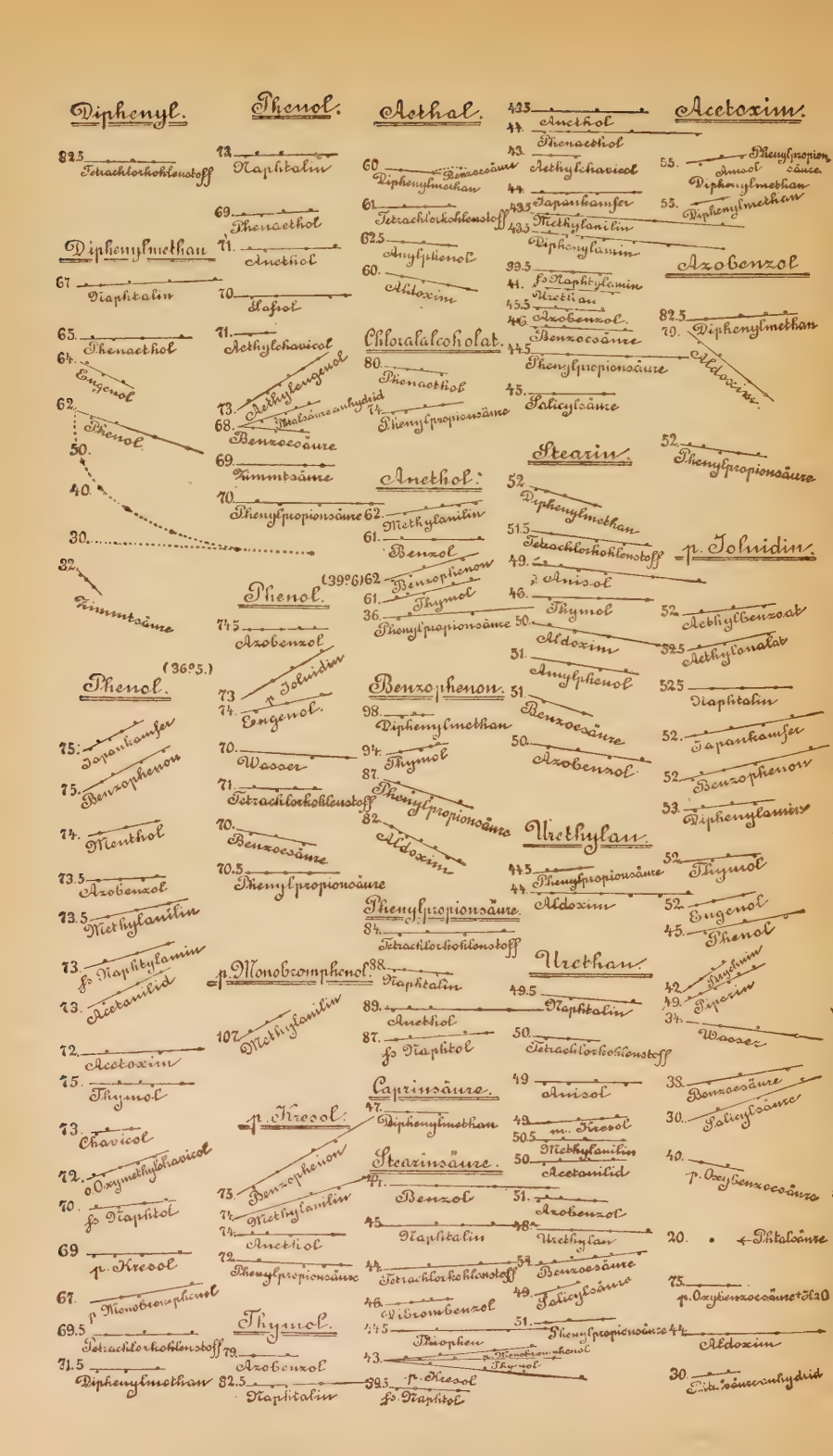
values. Relations different from those which hold good in other cases evidently prevail here. One will not go wrong in regarding solutions of these oxims in benzene as analogous with the vapour of nitrogen peroxide at a moderate temperature. Most of the molecules in dilute solutions, on the one hand, and at small pressures, on the other hand, exist as simple molecules; the greater the concentration, or the greater the pressure, the more do the molecules combine to form double molecules.

Not many substances show a behaviour of this kind. Eykman has examined a very great number of substances in very different solvents; the results of his measurements are represented on the next page by the same method as is employed in figs. 30 to 34. The names with two lines beneath denote the solvents, the others denote the dissolved substances.[1] The numbers express the constant K of Raoult's equation, determined from the observed lowerings of freezing-point and the molecular weights (taken as known) of the dissolved substances. Almost all the curves are seen to be straight lines.

This investigation shows that the best approximations to the true molecular weights are obtained by prolonging the lines which represent the observed values as far as the axis of the ordinates, and regarding the portions which are cut off, that is, the molecular weights at infinite dilution, as correct. This result might be foreseen, inasmuch as the theory of van 't Hoff gives only approximate results for finite concentrations, and can be accepted as strictly correct only for infinitely small concentrations.

12. **Theory of the deviations.**—As one gram-molecular weight of a gas at 0° and 760 mm. pressure occupies 22·4 litres, so the osmotic pressure which prevails in a solution of the same quantity in 1 litre amounts to 22·4 atmospheres. Now the compound gases of simple composition show marked deviations from the gaseous laws at such pressures as this, and similar deviations, but to a greater degree, are

[1] See footnote on p. 233.



Diphenyl.

82.5 Tetrachlorkohlenstoff

Diphenylmethan

67 Naphtalin

65. Phenaethol

64. Eugenol

62. Phenol

50.

40.

30.

32. Zimmtsäure

Phenol. (36°5.)

75. Japankamfer

75. Benzophenon

74. Menthol

73.5 Azobenzol

73.5 Methylanilin

73. fs Naphtylamin

73. Acetanilid

72. Acetoxim

75. Thymol

73. Chavicol

72. o. Oxymethylchavicol

70. fs Naphtol

69 p. Kresol

67. p Monobromphenol

69.5 Tetrachlorkohlenstoff

71.5 Diphenylmethan

Phenol.

73. Naphtalin

69. Phenaethol

71. Anethol

70. Safrol

71. Aethylchavicol

73. Aethylengenol

68. Phtalsäureanhydrid

Benzoesäure

69. Zimmtsäure

70. Phenylpropionsäure

Phenol.

74.5 Azobenzol

73 p. Joluidin

74. Eugenol.

70. Wasser

71. Tetrachlorkohlenstoff

70. Benzoesäure

70.5 Phenylpropionsäure

p. Monobromphenol.

107 Methylanilin

p. Kresol.

75. Benzophenon

74. Methylanilin

74. Anethol

72. Phenylpropionsäure

Thymol.

79. Azobenzol

82.5 Naphtalin

Aethal.

60 Benzoesäure

Diphenylmethan

61. Tetrachlorkohlenstoff

62.5 Amylphenol

60. Aldoxim

Chloralalcoholat.

80. Phenaethol

74. Phenylpropionsäure

Anethol.

62. Methylanilin

61. Benzol

(39°6) 62 Benzophenon

61. Thymol

36. Phenylpropionsäure

Benzophenon.

98. Diphenylmethan

94. Thymol

87. Phenylpropionsäure

82. Aldoxim

Phenylpropionsäure.

84. Tetrachlorkohlenstoff

88. Naphtalin

89. Anethol

87. fs Naphtol

Caprinsäure.

47. Diphenylmethan

Stearinsäure.

41. Benzol

45. Naphtalin

44. Tetrachlorkohlenstoff

46. Dibrombenzol

44.5 Thiophen

43. p. Monobromphenol

Thymol

p. Kresol

39.5 fs Naphtol

43.5 Anethol

44. Phenaethol

43. Aethylchavicol

44. Japankamfer

43.5 Methylanilin

43.5 Diphenylamin

39.5 fs Naphtylamin

41. Urethan

45.5 Azobenzol.

46. Benzoesäure

44.5 Phenylpropionsäure

45. Salicylsäure

Stearin.

52. Diphenylmethan

51.5 Tetrachlorkohlenstoff

49. Anisol

46. Thymol

50. Aldoxim

51. Amylphenol

51. Benzoesäure

50. Azobenzol

Urethylan.

44.5 Phenylpropionsäure

44. Aldoxim

Urethan.

49.5 Naphtalin

50. Tetrachlorkohlenstoff

49 Anisol

49. m. Kresol

50.5 Methylanilin

50. Acetanilid

51. Azobenzol

48. Urethylan

54 Benzoesäure

49. Salicylsäure

51. Phenylpropionsäure

Acetoxim.

55. Phenylpropionsäure

Anisol

Diphenylmethan

55. Diphenylmethan

Azobenzol

82.5 Diphenylmethan

79. Aldoxim

52. Phenylpropionsäure

p. Joluidin.

52. Aethylbenzoat

52.5 Aethylanalat

52.5 Naphtalin

52. Japankamfer

52. Benzophenon

53. Diphenylamin

52. Thymol

52. Eugenol

45. Phenol

42. Strychnin

49. Piperin

34. Wasser

38. Benzoesäure

30. Salicylsäure

40. p. Oxybenzoesäure

20. ← Phtalsäure

75. p. Oxybenzoesäure + öl 20

44. Aldoxim

30. Pitrosäureanhydrid

to be expected in the cases of the more complex substances with which we are now concerned.

As the behaviour of gases may be expressed, even to great pressures, with a near approximation to the truth, by the formula of van der Waals,

$$\left(p + \frac{a}{v^2}\right)(v - b) = \text{R T},$$

so it is possible, by using a similar formula, to calculate the deviations from the simple laws which are shown by solutions. After I, led thereto by the results of electrical measurements, had pointed out the need of looking at these secondary actions in the way referred to already,[1] the necessary calculations were furnished by Bredig [2] and A. Noyes.[3] The demonstration of the last-named author is given here.

Let p be the osmotic pressure, and v be the volume, of a solution which contains one gram-molecular weight of a substance; let B be the molecular volume of the dissolved substance, in the ordinary meaning of the term, b the space occupied by the molecules of the dissolved substance, and c the space occupied by the molecules of the solvent, referred to the unit-volume of the same. Then the correction to be made for volume, corresponding with the formula of van der Waals, is $b + (v - \text{B})\, c$. The correction for pressure is proportional to, on one side, $\frac{1}{b}$, and on the other side, $\frac{v - \text{B}}{v}$; if a is the corresponding constant for the attraction, the corresponding value may be put as $\frac{a}{v} \cdot \frac{v - \text{B}}{v}$, and we have

$$\left(p - \frac{a}{v} \cdot \frac{v - \text{B}}{v}\right)(v - [b + (v - \text{B})\, c]) = \text{K}, \text{ or}$$

$$\left(p - \frac{a\,(v - \text{B})}{v^2}\right)(1 - c)\left(v - \frac{b - \text{B}\,c}{1 - c}\right) = \text{K}.$$

[1] *Zeitschr. f. physikal. Chemie*, **2**, p. 280 [1888].
[2] *Ibid.* **4**, p. 444 [1889]. [3] *Ibid.* **5**, p. 53 [1890].

Now B is small as regards v, and as $\frac{a}{v}$ is small as regards p, we may put $\frac{v - B}{v} = 1$. Hence it follows that

$$\left(p - \frac{a}{v}\right)\left(v - \frac{b - Bc}{1 - c}\right) = pv - a - p\frac{b - Bc}{1 - c} + \frac{a}{v}\frac{b - Bc}{1 - c} = \frac{K}{1 - c}.$$

In the term $\frac{a}{v} \cdot \frac{b - Bc}{1 - c}$, which is not large, $\frac{a}{v}$ may be replaced, in accordance with the simple gaseous law, by $a_1 p$, where a_1 is a new constant; we thus arrive at the formula

$$p\left\{v - (1 - a_1)\frac{b - B}{1 - c}\right\} = \frac{K}{1 - c} + a,$$

or, by introducing two new constants, $(1 - a_1)\frac{b - Bc}{1 - c} = d$ and $\frac{K}{1 - c} + a = K_1$, we have

$$p(v - d) = K_1.$$

The simplifications which have been made have led to a form of the equation which regards the pressure-forces due to the interactions of the molecules as absent, and takes cognisance only of a correction for volume. It has been shown that a formula similar to this is in keeping with the facts concerning gases.[1]

To make this formula applicable to observations of freezing-points, it is only necessary to remember that the lowering of freezing-point, Δ, is proportional to the osmotic pressure. If v has the same meaning as before, the product $\Delta(v - d)$ must be constant. As d is to be found from the experimental results, it is calculated from two observations which have given corresponding values, Δ_1 and v_1, Δ_2 and v_2; $\Delta_1(v - d) = \Delta_2(v_2 - d)$;

$$d = \frac{\Delta_1 v_1 - \Delta_2 v_2}{\Delta_1 - \Delta_2}.$$

[1] Reference is made here in the original to an earlier chapter in the *Lehrbuch.—Translator.*

An example is given to show in how far the formula is in keeping with the observed results:—

Acetone in Benzene (Beckmann).

Δ	v	Δv	$\Delta (v-d)$	Deviation
0·405	14·010	5·674	5·700	+·0021
1·220	4·594	5·606	5·684	+·0005
3·615	1·507	5·448	5·679	0·0000
5·365	0·992	5·322	5·666	—·0013
8·470	0·609	5·157	5·686	+·0007

The mean value of $\Delta (v - d)$ is 5·679, and the mean value found for d is ·064. The last column shows that the deviations, as far as the first doubtful number, do not exceed 2 per thousand. The agreement is equally good in a great many other measurements. As an example, the numbers obtained in a series of experiments with chloral hydrate are appended; the solution used for the last measurement contained about 35 per cent. of the substance.

Chloral Hydrate in Water (Beckmann).

Δ	v	Δv	$\Delta (v-d)$	Deviation
0·775	2·596	2·012	1·942	+·001
1·365	1·506	2·055	1·932	—·009
1·915	1·097	2·101	1·929	—·012
3·145	0·705	2·216	1·933	—·008
4·165	0·5585	2·326	1·951	+·010
5·350	0·4564	2·442	1·960	+·017
6·120	0·4074	2·495	1·943	+·002

The value of d was found to be ·09; while Δv increases from 2·01 to 2·5, i.e. by a fourth of its value, $\Delta (v - d)$ remains constant to within a half per cent.

We have still to inquire into the meaning of the constant d. The value of this constant is sometimes positive and sometimes negative; but a negative volume is unthinkable.

We have

$$d = \frac{1 - a_1}{1 - c}(b - \text{B}\, c);$$

the factor $\frac{1 - a_1}{1 - c}$ is always positive, hence the sign of d will agree with that of $b - \text{B}\,c$. Now b is the volume of the ponderable substance of the molecules of the dissolved substance, and $\text{B}\,c$ is the corresponding volume of the molecules of the solvent in the same exterior space; for B is the molecular volume, as this term is commonly used, of the dissolved substance, and c is the space occupied by the molecules of the solvent, in the unit of space. The quantities b and $\text{B}\,c$ are not known immediately. But if we take b_0 and b_1 as the volumes of one molecule of the solvent and the dissolved substance, respectively, and A_0 and A_1 as the relative number of these molecules in the unit of space—or the quotients of the specific gravities by the molecular weights—then we can substitute b and $\text{B}\,c$ by the proportional values $b_1\,\text{A}_1$ and $b_0\,\text{A}_0$. By working this out, and combining all unknown quantities into one constant X, we obtain the equation

$$\frac{d_1}{\text{B}_1}\text{X} = \text{A}_1 b_1 - \text{A}_0 b_0,$$

and for a second substance

$$\frac{d_2}{\text{B}_2}\text{X} = \text{A}_2 b_2 - \text{A}_0 b_0;$$

hence

$$\frac{d_1}{\text{B}_1} - \frac{d_2}{\text{B}_2} = \text{A}_1 b_1 - \text{A}_2 b_2.$$

This equation enables conclusions to be drawn, under certain conditions, as to which of the molecules that are compared is the greater. Inasmuch as X is positive, both differences have the same sign. Now let the left side of this equation be positive, then $\text{A}_1 - \text{A}_2$ will be negative. It is therefore necessary that b_1 should be greater than b_2, as otherwise the difference $\text{A}_1 b_1 - \text{A}_2 b_2$ could not be positive. On the other hand if $\text{A}_1 - \text{A}_2$ is positive, no conclusion can be drawn as to the relative magnitudes of b_1 and b_2. In the same way, if the left side of the equation is negative and $\text{A}_1 -$

is positive, it is necessary that $b_1 < b_2$; if both sides of the equation have the same sign, no conclusion can be drawn. The equation $\frac{d_1}{B_1} x = A_1 b_1 - A_0 b_0$ may be treated in exactly the same way.

In the case of the solutions in benzene, the 'irreducible' case seldom occurs, and by determining, in the way described, which molecules are greater than others, the following order is obtained:

Acetone < benzene < acetophenone < acetal < camphor < ethyl benzoate < naphthalene < benzaldehyde < nitrobenzene < benzophenone < phenetol.

The mutual relations of these compounds have been determined independently in several cases (generally six), and no deviation has been found in any case. The method of procedure may then be regarded as a suitable one, and as well fitted for setting forth the facts.

13. **The molecular weights of dissolved substances.**—The use of the law which has been set forth in preceding paragraphs is sometimes opposed on the ground that it does not always lead to the 'proper' molecular weight. For instance, the molecular weight of acetic acid dissolved in benzene was found by Raoult to be 120, which is twice that required by the formula $C_2H_4O_2$; therefore, it has been argued, benzene is not a suitable solvent when the molecular weight of acetic acid is to be determined. The supposition which underlies this argument is that a specified substance can have but one molecular weight; but this supposition is quite ·oneous. Even when attention is confined to the classical Th hod of determining molecular weights, the method of fr ur densities, it is necessary to admit that the value of rei molecular weight of one and the same substance is etimes dependent on the temperature and pressure. d. ogen peroxide, for instance, has the molecular weight sor nd the formula N_2O_4, at low temperatures and great sures, and at high temperatures and small pressures it the molecular weight 46 and the formula NO_2. In the

same way, we know that iodine, sulphur, and many other substances exist in two different molecular conditions.

It is not, then, to be wondered at that a definite substance should exhibit different molecular conditions when dissolved in different solvents. The different solvents act like different temperatures or pressures. So far as experiments have gone, it appears that hydrocarbons exert the smallest effect on the molecular state of the dissolved substance. Such hydroxyl compounds as acids, alcohols, phenols, &c., generally show greater molecular weights when dissolved in benzene than correspond with their accepted formulæ Naphthalene and ethylene bromide behave like benzene, while those compounds which show greater molecular weights in solutions in hydrocarbons generally give 'normal' values when dissolved in ether, the determinations being made by the method of vapour-pressure or boiling-point. Acetic acid exerts a more marked action in breaking down such weak combinations, and the action of water is still more energetic.

As it is essential for the chemist, at present, to be able to determine only the smallest of the possible molecular weights of the substances whose properties he examines, he will generally prefer water or acetic acid as a solvent, as in these solvents substances show molecular weights which agree, for the most part, with those determined by the method of vapour-density. The cases wherein greater molecular weights are found are, however, of especial importance in understanding the nature of chemical affinity, and the equivalency of atoms: for such cases throw light on those finer and weaker combinations which are almost invariably torn asunder, and, therefore, do not come into consideration, in the comparatively coarse processes of chemical change, although they certainly exist, and have an influence on these processes. If acetic acid, dissolved in benzene, has a molecular weight corresponding with the formula $2(C_2H_4O_2)$, then the molecules of pure liquid acetic acid are not smaller than this, although they may be greater. On the other

hand, ethylic acetate does not show, in any solvent, a molecular weight greater than the formula $C_4H_8O_2$ requires; hence it is probable, but not certain, that this compound does not possess any tendency to form more complex molecular aggregates, at the ordinary temperature, and therefore it is also probable that the liquid compound consists of molecules agreeing with the simple formula given above.

The results obtained by this way of looking at the matter show a remarkable agreement with those arrived at by Eötvös,[1] concerning the molecular state of certain substances, from measurements of surface-tensions. In alcohol and acetic acid he found molecules greater than corresponded with the ordinary formulæ. In water also, according to Eötvös, there are complex molecules. The same thing has been found by Eykmann [2] for solutions of water in paratoluidine, and by Walker [3] for solutions of water in ether.

14. **Cryohydrates.**—As the solubility of a substance in water generally decreases as temperature decreases, there must be, in most cases, a certain solution for each substance which is just saturated at the freezing-point. If such a solution is cooled, and supersaturation is prevented by addition of ice and solid substance, the substance in solution and ice must separate in the same proportion as that in which they are present in the solution; the temperature will remain unchanged until all is solidified. So on adding heat, the solid mixture will liquefy and the temperature will remain unchanged, as occurs with homogeneous substances, until all is melted.

Guthrie [4] gave the name *Cryohydrates* to the bodies produced in this way; he looked on them as chemical compounds because they possessed constant melting and

[1] *Wied. Ann.* **27**, p. 452 [1886].
[2] *Zeitschr. f. physikal. Chemie*, **4**, p. 510 [1889].
[3] *Ibid.* **5**, p. 197 [1890].
[4] *Phil. Mag.* (4) **49**, p. 1 [1875]; (5) **1**, p. 49; **2**, p. 211 [1876].

solidifying points and constant compositions. An investigation made by Offer [1] has shown, however, that there is no ground for regarding these substances as true compounds. The relations stated above account completely for the constancy of the melting-points and the composition; and the composition cannot be expressed quite accurately in accordance with atomic proportions. We have evidently to do with substances which are similar to the mixtures having constant boiling-points, spoken of on pp. 45, 46; it is also probable, although the matter has not yet been examined, that the composition of the cryohydrates, like that of the liquids referred to, is dependent on pressure, inasmuch as pressure exerts different effects on solubility and freezing-point.

Offer showed that the cryohydrates are not produced in well-formed translucent crystals, but always in opaque masses; that alcohol dissolves ice from them and leaves a network of solid salt; that the heat of solution of a cryohydrate is the sum of the heats of solution of the ice and salt which form it; and, lastly, that the specific gravity is equal to the mean specific gravity of the constituents. The third and fourth observations show that neither a volume-change nor a thermal change occurs in the formation of the cryohydrates; but these changes are never absent in the formation of true chemical compounds. The cryohydrates cannot, then, be regarded as chemical compounds.

These mixtures are particularly useful for maintaining constant temperatures below zero, inasmuch as by causing the melted part to solidify in a freezing-mixture the temperature may be kept at the melting-point of the cryohydrate for an indefinite time.

The peculiar properties of mixtures which were observed by Guthrie are completely explained by the mutual influence of the substances on their solubility.

The further developments made by Guthrie concerning the solubilities of salts below 0°, and the conception of

[1] *Wien. Akad. Ber.* **81** (2nd part), p. 1058 [1880].

unsaturated solutions as solutions of ice in cryohydrates, and of supersaturated solutions as solutions of salts in cryohydrates, may be passed over, as the observed facts may be predicted from our knowledge of the freezing of solutions.

CHAPTER IX

SALT-SOLUTIONS

1. Generalities.—Aqueous solutions of salts, and aqueous solutions of the strong acids and bases, differ in many respects from solutions of indifferent substances; the former, however, follow certain simple and definite laws, which do not hold good for the latter. It is evident, then, that aqueous salt-solutions present peculiar relations; the study of these forms the subject-matter of the present chapter.

It has been pointed out several times already that salts in solution behave as if the solutions contained a greater number of molecules than corresponds with the formulæ of the dissolved salts, and the conclusion has been drawn that these compounds are separated in their aqueous solutions into simpler constituents. The term 'salt' is used here, for the sake of brevity, as including the free acids and bases. Now in the case of such a salt as potassium chloride, the only simpler constituents are potassium and chlorine; hence an aqueous solution of this salt must contain both elements in the free state.

This conclusion, which was arrived at by Arrhenius,[1] and shortly afterwards (from quite different considerations) by Planck,[2] seems to be in glaring opposition to all experience. For potassium is a metal which cannot be in contact with water without decomposing the water violently, and chlorine is a greenish, strongly smelling gas. But none of

[1] *Zeitschr. f. physikal. Chemie*, 1, p. 631 [1887].
[2] *Ibid.* 1, p. 577 [1887].

these properties can be detected in a solution of potassium chloride.

Two replies may be made to this objection. The elements chlorine and potassium, as we know them, are molecular combinations, chlorine being composed of two atoms, and potassium of an unknown number of atoms. The chlorine and the potassium in solutions of potassium chloride are the elements in the atomic condition. Farther, the elements contained in a solution of potassium chloride are charged with enormous quantities of positive and negative electricity, respectively. This follows from the phenomena of electrolysis, which phenomena force us to the same conclusion as that now arrived at—to the conclusion, namely, that parts of the molecules, or ions, of salts are contained, like free molecules, in the solutions of these salts.

It must be clearly understood that this freedom exists only within the solutions; the removal of an ion from the solution is at once opposed by molecular and electrical forces of considerable magnitude. The development of these relations belongs to another place; it will suffice to say here that the conclusions which follow from the theory of solutions are the same as those which are necessarily arrived at by following the theory of electrolysis. While, therefore, I do not put forth here the proofs of the possibility, and the necessity, of the existence of free ions in the solutions of salts, I shall develope the conclusions which follow from this supposition.

The most general conclusion to be drawn from the hypothesis of free ions is that *the properties of salt-solutions must be capable of representation as the binary sums of the properties of the two ions.*[1] As the ions are not in immediate combination with one another, no mutual determination of the properties of the ions occurs, and as far as the effect of one ion on the total properties is concerned, it does not matter what other ion is present at the same time

[1] Arrhenius, *Zeitschr. f. physikal. Chemie*, 1, p. 631 [1887].

in the solution. But it must be clearly understood that this conclusion has reference only to the limiting case that the whole of the dissolved salt has separated into ions. This occurs, theoretically speaking, only in infinitely dilute solutions. In actual practice, solutions of salts more nearly agree with the general law stated above, the more dilute they are. It is found that many salts are separated to such a great extent into their ions in solutions of moderate dilution that the additive character of their properties comes into view in a very clear way.

2. **Chemical properties of salt-solutions.**—Before considering the physical properties of salt-solutions it will be well to recall the additive character of their chemical properties.[1] Chemical compounds generally show behaviours that are characteristic of each, but these allow conclusions from analogy to be drawn only in departments that are closely allied, and even in these cases they do not exhibit regular agreements. We do not know why the chlorine compounds of carbon belong to the most stable compounds, especially in their indifference towards the action of water, while nitrogen chloride explodes under the smallest provocation, although it is not decomposed by water, and silicon chloride is decomposed rapidly by water, although it withstands the action of heat; conclusions, drawn from the characters of the chlorides of carbon, regarding the chlorides of the allied elements silicon and titanium, would lead us into error, as certainly as conclusions regarding the chlorides of phosphorus and arsenic, drawn from the properties of the chloride of the allied element nitrogen, would be erroneous.

The regularities shown by the chemical reactions of aqueous solutions of salts stand in the most marked opposition to these differences. If barium compounds in solution produce a white precipitate in a solution, which precipitate is insoluble in hydrochloric acid, we are as sure that sulphates are present as we should be certain of their

[1] Ostwald, *Zeitschr. f. physikal. Chemie*, 3, p. 596 [1889].

absence did no precipitate form. The nature of the metal with which the sulphuric acid was in combination does not exert the least influence, qualitatively or quantitatively, on the result. The same state of matters holds good in all analytical reactions. The law of the mutual independence of the constituents of salts in solution becomes very prominent in these occurrences. There is no reagent for detecting sodium chloride; the reagents used detect only chlorine and sodium; and these reagents are effective for all solutions in which chlorine, on the one hand, and sodium, on the other hand, are present as ions.

A substance which is not present as an ion ceases to show the characteristic reactions of that substance. Silver is a reagent for chlorine, but silver does not show the presence of chlorine in the perchlorates. This is because the ions of these salts are, e.g., K and ClO_4; chlorine is not an ion of the perchlorates, and these salts, therefore, do not show the reactions of chlorine. But if a perchlorate is changed into a chloride by heat, a solution of the chloride shows the chlorine-reactions because chlorine ions are now present.

3. **Specific gravity and specific volume.**—The specific gravities of many salt-solutions have been determined with great care, with the object of furnishing aids of the simplest kind in analysis, because such salt-solutions are much used both in the laboratory and in manufacturing operations. As the specific gravities of such solutions, generally speaking, are direct functions of the contents of the solutions, it is easy to find the contents when the specific gravity is known.

The customary representation of the relation between space and mass in the form of *specific gravity* has made difficult, and tended to put aside, the comprehension of this relation. For in the simplest case, where no volume-change occurs on mixing a concentrated solution with water, the specific gravity of the mixture bears no simple relation to the specific gravities of the constituents. Let s be the

specific gravity of the concentrated solution, and s_0 that of the pure solvent. If we mix m parts of the solution with m_0 parts of the solvent, then, on the supposition that no change of volume occurs, the total volume of the mixture is $\frac{m}{s} + \frac{m_0}{s_0}$, and as the total weight is $m + m_0$, the specific gravity of the mixture is given by the somewhat obscure expression

$$\frac{(m + m_0)\, s\, s_0}{m\, s_0 + m_0\, s}.$$

But if use is made of the specific volume, simple formulæ are obtained. Let ϕ be the specific volume of the solution, and ϕ_0 that of the solvent, m and m_0 being the parts of each, then the specific volume of the mixture is $\frac{m\,\phi + m_0\,\phi_0}{m + m_0}$, which corresponds with the ordinary mixture-formula. If the supposition that the mixture takes place without volume-change is not fulfilled, then the difference between the specific volume calculated as above and the observed specific volume furnishes a direct survey of the direction and value of the volume-change, which survey can be gained only by a somewhat complex calculation when the notion of specific gravity is employed.

As regards the question of the volume-changes which occur on diluting concentrated salt-solutions, it has been known for long that such dilution is accompanied by contraction, i.e. by decrease of volume. This effect is most marked when concentrated solutions are used, and it decreases the more the greater the dilution. If a concentrated salt-solution is diluted to twice its volume, and the same degree of dilution is repeated with the dilute solution, and so on, the volume-changes which occur are smaller the farther the dilution is carried. And this holds good not only for equal quantities of the differently concentrated solutions, but also for those in which the same weight of salt is always present, and in which, therefore, the observed total volume increases on dilution.

These relations were called into question, for a time, by an investigation of Michel and Krafft,[1] who asserted, but on insufficient grounds, that no change of volume occurs when salt-solutions are diluted. Kremers,[2] who had clearly demonstrated such volume-changes, soon contradicted this assertion, and subjected the questions regarding the specific gravities of salt-solutions to very full experimental examination. Kremers did not arrive at any very clear results, because of an inappropriate method of considering the data, but he gathered together many measurements which, when properly treated, lead to important results.

At a later time Nicol[3] considered the changes of volume which accompany the dilution of salt-solutions with reference to stoïchiometrical considerations, but without any very special results. Nicol thought he had discovered a connexion between the volume-changes and the solubility of the salt in solution, but the data were too scanty to establish his statement with certainty.

It is sufficient here to refer to the work of Charpy,[4] which indicated certain stoïchiometrical relations.

Finally, the following facts should be mentioned. If the volume of the water in a salt-solution which contains a specified amount of a salt is deducted from the volume of the solution, the result gives the apparent volume of the salt in solution. It follows from what has been said already that this volume will be the less the greater the quantity of water, and that it will asymptotically approach a limit as dilution increases. Now, it is observed that the apparent volume of the salt in solution, in certain cases, may pass through zero and become negative, so that the solution may at last attain a smaller volume than that of the water which has been employed in making the solution.

This fact is of interest in so far as it shows that the volume-change which occurs on dilution does not affect the

[1] *Ann. Chim. Phys.* (3) **41**, p. 471 [1854].
[2] *Pogg.* **95**, p. 110; **96**, p. 39 [1855].
[3] *Phil. Mag.* (5) **16**, p. 121 [1883]. [4] *Compt. rend.* **109**, p. 299 [1839].

salt only, but that reactions occur between the molecules of the salt and those of the water, which, in turn, result in a decrease of volume. The apparent volume of the salt in solution, as defined above, is the difference between the true volume of the salt and the change of volume which is brought about by the reaction between the salt and the water. As the true volume of the salt cannot be negative, the fact that the difference may have a negative value shows that the change of the volume of the water, caused by the dissolved salt, has a value comparable with, and under certain conditions exceeding, the true volume of the salt.

4. **Valson's law of the moduli.**—The first observations regarding the stoïchiometrical relations of salt-solutions were made by F. Valson ;[1] the method was the inconvenient one of considering the specific gravities of the solutions, which had already been employed by Kopp in other inquiries. If solutions of various salts, each containing one gram-equivalent per litre, are considered, it is found that the differences between the specific gravities of solutions which contain two specified metals in combination with the same acid have an equal value, whatever be the acid, and, similarly, that the differences between the specific gravities of the solutions of two salts of the same acid are independent of the nature of the metal of the salts. The specific gravity of a salt-solution is obtained by adding, to a normal value, two numbers, one of which is determined by the metal and the other by the acid. Valson called these numbers *moduli*. He selected a liquid of very low specific gravity, viz. solution of ammonium chloride with S.G. 1·015, as the standard solution. It would have been better had he chosen water ; it would then have been necessary to increase one series of *moduli* by 15. Valson's table is appended ; the numbers are referred to *equivalent* quantities (H = 1), e.g. Mg is calculated as 12·2 and not as 24·4. The numbers are multiplied by 1,000.

[1] *Compt. rend.* 73, p. 441 [1874].

Ammonium	0	Cadmium	61
Potassium	30	Lead	103
Sodium	25	Silver	105
Calcium	26	Chlorine	0
Magnesium	20	Bromine	34
Strontium	55	Iodine	64
Barium	73	Sulphate	20
Manganese	37	Nitrate	15
Iron	37	Carbonate	14
Zinc	41	Bicarbonate	16
Copper	42		

To find the specific gravity of a normal solution of potassium nitrate, for instance, it is necessary to add to the standard number, 1·015, the number ·03 for potassium, and ·015 for nitric acid; the result is 1·06, which agrees with the experiments. The rule holds only for dilute solutions. An extension has been made to solutions of any concentration by C. Bender.[1] This investigator divided the differences of specific gravities by the number of equivalents, and found that the quotients agreed with Valson's moduli. In other words, he found that the difference between the specific gravities of the solutions of two substances containing equal numbers of gram-equivalents in a litre[2] was proportional to the number of the equivalents. The following table illustrates this rule; μ is the number of equivalents, and Δ is the difference of specific gravities :—

μ	NH_4Cl	KCl	$KCl\frac{\Delta}{\mu}$	$NaCl\frac{\Delta}{\mu}$	$LiCl\frac{\Delta}{\mu}$	$\frac{1}{2}BaCl_2\frac{\Delta}{\mu}$
1	1·0157	1·0444	287	244	78	738
2	1·0308	1·0887	289	240	78	736
3	1·0451	1·1317	289	238	—	732
4	1·0587	—	—	234	79	—
5	1·0728	—	—	232	76	—

The specific gravities of solutions of NH_4Cl and KCl are given in the table, only the differences are shown for

[1] *Wied. Ann.* **20**, p. 560 [1883].

[2] Bender did not consider solutions containing one gram-equivalent in one litre of water, but those which contained one or several equivalents per litre of the whole solution.

the other salts. The differences divided by the number of equivalents are placed under KCl $\frac{\Delta}{\mu}$. The other columns contain values for other salts calculated in the same way, all being compared with sal-ammoniac. Almost all the quotients decrease as μ increases; but this depends only on the choice of the liquid for comparison—had NaCl been chosen the quotients would have remained more nearly constant. The quotients $\frac{\Delta}{\mu}$ are the *moduli* of Valson. The specific gravity of any solution containing μ equivalents in a litre is, then, obtained by adding the *moduli* of the salt, multiplied by μ, to the specific gravity of a solution of sal-ammoniac which contains the same number of equivalents. The following values for the *moduli* were obtained by Bender; they hold good at 18° :—$NH_4 = 0$, K = 296, Na = 235, Li = 72, $\frac{1}{2}$Ba = 739, $\frac{1}{2}$Sr = 522, $\frac{1}{2}$Ca = 282, $\frac{1}{2}$Mg = 221, $\frac{1}{2}$Zn = 410, $\frac{1}{2}$Cd = 606, $\frac{1}{2}$Cu = 413, $\frac{1}{2}$Ag = 1069, Cl = 0, Br = 370, I = 733, $NO_3 = 160$, $\frac{1}{2}SO_4 = 200$.

To take an instance: it is required to find the specific gravity of a solution of calcium bromide containing 3 equivalents per litre. To the specific gravity of the corresponding solution of sal-ammoniac, viz. 1·0451, add 3 (·0282 + ·037) = ·1956; the result is 1·2407; the number observed by Kremers was 1·2395. The specific gravities of sal-ammoniac solution are

n	S.G.
1	1·0153
2	1·0299
3	1·0438
4	1·0577

One must not deceive oneself as to the consequences of these results. The stoïchiometrical law on which they are based is not set forth clearly; the method is not a rational one, inasmuch as it does not rest upon simple and present-

able conceptions. It was pointed out before, that the notion of specific gravity is not suited for representing stoïchiometrical laws, because the quantities dealt with are not comparable; the conception of specific, or molecular, volume should be employed. The extension of Valson's law to solutions of different concentrations is made possible by the fact that equivalent salt-solutions contract nearly equally on dilution. The magnitude of the contraction is unimportant; a mean value is easily found which leads to results that are more in keeping with experiment than those calculated on the arbitrary assumption that all salt-solutions contract to the same extent as solution of ammonium chloride.

The reason for the observed regularities which, as has been said, afford only a somewhat distorted representation of the true laws regarding the molecular volumes of salt-solutions, is to be found in the regular volume-changes which accompany the formation of salts in aqueous solutions. Before considering these volume-changes, notice should be taken of an investigation made by Groshans[1] in which an addition is made to the molecular method of regarding the phenomena. Groshans found that the difference between the molecular volume of a salt-solution and that of the water in the solution decreases as the quantity of water increases, but approaches a limit asymptotically. This limit of the difference which may be regarded as the molecular volume of the dissolved salt, was determined by help of an interpolation-formula, $d = 1 + \frac{\alpha}{w + \beta}$, where $d =$ specific gravity, $w =$ quantity of water referred to unit quantity of the salt, and α and β are constants. The limiting values thus obtained show a close correspondence with Valson's law of the moduli, for they are found to be the sums of two constants, one of which is determined by the acid and the other by the base. The farther development made by Groshans is not based on those limiting values, or 'rests,'

[1] *Wied. Ann.* 20, p. 492 [1883].

as he calls them, but on the values of the quantity a, which is defined by the relation $r = a\,(1 - a)$, where r = the 'rest' and a = the molecular weight of the salt. This quantity has rather a complicated signification; it is the amount by which the specific volume of the 'rest' is less than unity. The further conclusions of Groshans become unreal; they are algebraical relations without physical significance. The unsuitability of specific gravity to stoïchiometrical considerations becomes evident once more; had the author kept to the consideration of molecular volumes, and had he not brought in the quantity a in place of the specific gravity formula, his determinations of the volume-components of infinitely dilute salt-solutions would have been of great stoïchiometrical interest.

5. **Changes of volume in chemical processes.**—Valson's law of moduli bears a very close relation to the volume-changes which accompany chemical processes occurring in aqueous solutions. In 1859, Gerlach [1] announced the important fact that expansion, and not contraction, occurs when a solution of potash is neutralised by dilute acids. After this, Tissier [2] carried out experiments on the subject. Inasmuch as the chief results of this meritorious work do not belong to our present purpose, they are not given here. It may be mentioned, however, that Tissier established by direct experiments the expansion of alkali solutions on neutralisation which had been deduced by Gerlach by calculation. Solutions of ammonia showed contraction. Tissier explained this by supposing that water is formed when potash or soda is neutralised, but not when ammonia is neutralised. But it is to be noted that the volume-increase in the former cases is greater than the volume of the water formed, and that the atoms which formed water could not be supposed to have occupied no space before the neutralisation.

At a later time J. Regnauld [3] published some similar

[1] *Salzlösungen* (1859), p. 73. [2] *Jahresber.* 1859, p. 45.
[3] *Ibid.* 1865, p. 69.

measurements which, on the whole, confirmed the former results: expansion occurred on neutralisation of potash, soda, baryta, and thallium oxide; contraction occurred with ammonia and ethylamine. Regnauld's explanation was the same as that given by Tissier.

An extended investigation of the volume-changes which accompany the neutralisation of solutions of potash, soda, and ammonia, by various acids, led me [1] to stoïchiometrical relations, which make clear the cause of the law of Valson. The solutions employed contained one gram-equivalent of the base, or acid, in one kilogram; the changes of volume are expressed in cubic centims. It appears that the volume-change is dependent on the nature both of the acid and of the base, but that the *difference* of the volume-changes which accompany the neutralisation of two different bases by one and the same acid is the same whatever acid is used. In the same way, the difference in the neutralisation of any acids by the same base is independent of the nature of the base. The following table represents the relations in question:—

VOLUME-CHANGES ACCOMPANYING NEUTRALISATION.

	Potash	Diff.	Soda	Diff.	Ammonia	Diff.
Nitric acid . . .	20·05	·28	19·77	26·21	−6·44	26·49
	(·53)		(·53)		(·13)	
Hydrochloric acid . .	19·52	·28	19·24	25·81	−6·57	26·09
	(·42)		(·43)		(·13)	
Hydrobromic „ . .	19·63	·29	19·34	25·91	−6·57	26·20
	(·25)		(·23)		(·00)	
Hydriodic „ . .	19·80	·26	19·54	25·98	−6·44	26·24
	(7·69)		(7·64)		(7·15)	
Formic „ . .	12·36	·20	12·16	25·75	−13·59	25·95
	(10·53)		(10·49)		(9·82)	
Acetic „ . .	9·52	·24	9·28	25·55	−16·26	25·78
	(9·19)		(9·14)		(8·65)	
Monochloracetic acid .	10·86	·23	10·63	25·72	−15·09	25·95
	(7·10)		(7·07)		(8·45)	
Dichloracetic „ .	12·95	·24	12·70	25·68	−12·98	25·92
	(2·69)		(2·70)		(2·23)	
Trichloracetic „ .	17·36	·29	17·07	25·74	−8·67	26·03
	(12·22)		(12·09)		(11·38)	
Propionic „ .	7·83	·15	7·68	25·50	−17·82	25·65

[1] *J. für prakt. Chemie* (2), **18**, p. 353 [1878].

VOLUME-CHANGES ACCOMPANYING NEUTRALISATION.

	Potash	Diff	Soda	Diff.	Ammonia	Diff.
	(13·07)		(12·93)		(12·19)	
Butyric acid . .	6·98	·14	6·84	25·47	−18·63	25·62
	(13·75)		(13·60)		(12·83)	
Isobutyric „ . .	6·30	·13	6·17	25·44	−19·27	25·57
	(10·43)		(10·25)		(10·06)	
Glycolic „ . .	9·62	·10	9·52	26·02	−16·50	26·12
	(11·78)		(11·64)		(11·30)	
Lactic „ . .	8·27	·14	8·13	25·87	−17·74	26·01
	(8·15)		(8·29)		(7·91)	
Sulphuric „ . .	11·90	·42	11·48	25·83	−14·35	26·25
	(10·16)		(10·02)		(9·68)	
Oxalic „ . .	9·89	·14	9·75	25·87	−16·12	26·01
	(11·82)		(11·84)		(11·19)	
Succinic „ . .	8·23	·30	7·93	25·56	−17·63	25·86
	(11·43)		(11·27)		(11·00)	
Malic „ . .	8·62	·12	8·50	25·94	−17·44	26·08
	(10·64)		(10·53)		(10·52)	
Tartaric „ . .	9·41	·17	9·24	26·20	−16·96	26·37

The numbers in the column headed 'Diff.' represent the volume-changes of potash *minus* soda, soda *minus* ammonia, and potash *minus* ammonia. The numbers in brackets placed above the values of the volume-changes represent the differences between the acid, in each case, and nitric acid. It is evident that the differences in the vertical columns, and the differences (in brackets) in the horizontal columns, remain nearly constant. The results also show the limits within which the law holds good, and make it clear that this law, like so many others, is only approximately correct.

Similar laws hold good, as has been pointed out already, for very many other properties, both of solutions and of simple substances. All such laws may be expressed thus: *the changes of properties which occur in chemical processes between analogous salts are composed, additively, of two constants, one of which belongs to one component and the other to the other component; and each of these constants is independent of the substance with which the component may react.* In the especial case under consideration, the volume-change is the sum of two changes, one of which is dependent only on the acid and the other only on the base. It is possible

that a third quantity is to be added to the sum of these two, which is independent of the two components and is conditioned only by the nature of the chemical change, which, in the present case, is formation of salts; the third quantity must have a constant value. If the parts contributed by the acids to the total volume-change be represented by a, a', a'' . . . . , and the parts contributed by the bases by b, b', b'', ... , and if c be the constant dependent on the nature of the change, then the following schematic table gives a systematic arrangement of the volume-changes :—

$a + b + c$	$a' + b + c$	$a'' + b + c$	. . .
$a + b' + c$	$a' + b' + c$	$a'' + b' + c$	. . .
$a + b'' + c$	$a' + b'' + c$	$a'' + b'' + c$	. . .
. . .	. . .	. . .	

The differences are here subjected to the same law as was found to hold good for the experimentally determined volume-changes: each term in a horizontal series deducted from the corresponding term in another horizontal series gives the same value, and the same value is also obtained by deducting any term in a vertical series from the corresponding term in any other vertical series.

The connexion between these relations and Valson's *law of moduli* is obvious. The volume-change which occurs when a base is neutralised by different acids, consists of a constant part belonging to the base, and a changeable part which has a definite value for each acid; i.e. the volume of the solution which is produced is the sum of two parts, one depending on the base and the other on the acid. What holds good for the volumes also holds good, although less rigorously, for their reciprocals, the densities. As the volumes do not differ much from unity, the approximate method of calculation may be used, wherein α and β being small numbers, $\frac{1}{1 + \alpha + \beta}$ is put as equal to $1 - \alpha - \beta$.

The fact that the volume of a salt-solution is equal to the sum of two volume-constants which belong to the two

ions of the salt in solution, has been discussed more fully of late years, especially by Nicol,[1] but no important new developments have been made. Measurements of the volume-components, corresponding with Valson's *moduli*, have not been made for any wide range of substances. Nicol's observation [2] deserves notice, that there seems to be a constant difference between the volumes of equivalent solutions of the sodium salts of the fatty acids as an homologous series of these acids is ascended. The following numbers were obtained for the volumes of Na $A + 100\ H_2O$ at 20° :—

		Δ
Formate	1825·2	. —
Acetate	1840·1	14·9
Butyrate	1867·5	13·7 × 2

It is likely that relations will be found in such cases which will resemble those that prevail for the molecular volumes of organic compounds.

6. **Thermal expansions of solutions.**—Inquiry into the changes which aqueous solutions of salts undergo when heated has accompanied the development of trustworthy methods for finding the specific gravities of these solutions; but the subject has scarcely advanced beyond finding empirical and practical relations. Data have been accumulated by Bischoff, Muncke, and Despretz, for special cases of solutions of common salt and sea-water. The subject was taken up systematically by Gerlach,[3] and at the same time by Kremers;[4] to the latter we owe a large series of observations. Marignac also made investigations on this subject in 1870.

It may be said, generally, that the expansion of salt-solutions is the more uniform the more concentrated the solutions. While the volume-curve of water is much curved, that of a salt-solution more and more approaches a

[1] *Phil. Mag.* (5) **16**, p. 121 [1883]; **18**, p. 179 [1884].
[2] *Ibid.* (5) **16**, p. 131 [1883].
[3] *Spec. Gewichte der Salzlösungen*, Freiberg, 1859.
[4] *Pogg.* **100** to **120** [1857–62].

straight line. In consequence of this, solutions of salts expand to a greater extent at low temperatures than water; and as most salt-solutions show only a slightly greater volume-increase (and some show a smaller increase) than water up to 100°, the difference between the expansion-coefficients becomes smaller, and generally changes its sign before 100° is reached. There is, then, a temperature whereat the expansion-coefficient of a salt-solution is the same as that of water. According to M. P. de Heen,[1] this temperature is dependent only on the nature of the salt, and not on the concentration of the solution, and the following are the temperatures for some salts:—LiCl 30°, NH_4Cl 35°, NaCl 55°, KCl 50°, $MgCl_2$ 35°, $CaCl_2$ 45°, $BaCl_2$ 50°, $AlCl_3$ 37°, Na_2CO_3 67°, K_2CO_3 65°, NH_4NO_3 70°, KNO_3 70°, Na_2SO_4 60°, K_2SO_4 60°, $NaC_2H_3O_2$ 80°. The temperature increases with increase of atomic weight for similar salts, e.g. the alkali chlorides; in some other cases the temperature is the same.

This fact is very closely related to another which was discovered by Kremers at a much earlier date. If the volume of water in various salt-solutions is taken as 100, the values of the volumes of the solutions follow a characteristic course: they increase with increasing temperature, reach a maximum, and then decrease. The following table illustrates this behaviour; the numbers hold good for three equivalents in one litre of water:—

t	LiCl	NaCl	KCl	$\frac{1}{2}MgCl_2$	$\frac{1}{2}ZnCl_2$
0°	105·57	—	—	102·89	103·27
19·5	105·80 –	105·90	109·10	103·16	103·97
40	105·79	106·16	109·29 –	103·18 –	104·39
60	105·64	106·22 –	109·29	103·04	104·72
80	105·38	106·14	109·18	102·80	104·97
100	105·05	105·97	108·96	102·45	105·15

The numbers in the last column, $\frac{1}{2}ZnCl_2$, show that the behaviour is not universally the same.

[1] *Physique comparée*, Bruxelles, 1883, p. 76.

The numbers in this table may be taken as giving the volumes which are occupied by 100 c.c. of water, at different temperatures, when equal weights of different salts are dissolved therein. This volume at first increases as temperature rises, then reaches a maximum, and then decreases. If the excess over 100 be looked on as the volume of the dissolved salt at different temperatures, then this volume increases, attains a maximum, and decreases. The expansion-coefficient of the dissolved salt is equal to zero at the maximum, inasmuch as it changes from a positive to a negative value, and the expansion-coefficient of the solution, which is made up of the sum of the coefficients of water and the salt, agrees with that of water. A comparison of the results obtained by de Heen with those in the above table[1] shows a close agreement. Kremers also found that the temperature of maximum expansion is influenced by the concentration only to a very small extent.

The characteristic course which is followed by the (fictitious) volume of the dissolved salt is distorted to some extent in the tables of Kremers by an error of calculation. Kremers always puts the volume of the water at the specified temperature as 100, and he forgets that the numbers do not then refer to equal quantities of the solutions but to quantities which are related as the specific gravities of water. If the numbers in Kremers' tables are calculated rightly, the maximum appears as shifted for the most part to somewhat higher temperatures. In order to explain this anomaly, it is of course not necessary to assume that the salt contained in the solution really contracts with increasing temperature. As a matter of fact it expands. But, at the same time, the contraction which occurs during solution becomes greater as temperature rises, and the maximum is situated at the point where this begins to overcome the expansion which the salt itself undergoes by the heat; for it is not the volume of the dissolved salt that is observed, but this *minus* the contraction that occurs.

[1] *Pogg.* **106**, p. 382 [1858].

These relations have not yet been expressed in simple laws; Kremers' investigations [1] contain a rich collection of material for calculation.

A very extensive and accurate investigation of the specific gravities and thermal expansions of solutions of calcium chloride and sodium carbonate was published by G. J. W. Bremer.[2] As the observed regularities are confined to the special substances which were examined, it is enough for our purpose to give a reference to the original memoir.

7. **Compressibilities of salt-solutions.**—The older observations of Colladon and Sturm, and others, on the compressibilities of salt-solutions were not made from the stoïchiometrical standpoint, and they have no special application in that direction. Röntgen and Schneider [3] were the first to inquire into the subject in order to find stoïchiometrical relations; they determined the compressibilities of a number of comparable solutions, and obtained the following values for compressibility-coefficients. The numbers represent the *apparent* compressibilities, i.e. the compressibilities without taking into consideration the change of volume of the instrument; the apparent compressibility of water is taken as 1,000. The first table refers to solutions containing $1\frac{1}{2}$ gram-molecules of each salt per litre; the second refers to ·7 normal solutions.

1·5 Normal Solutions.

	H	NH_4	Li	K	Na
I	—	910	888	869	863
NO_3	958	908	870	863	853
Br	960	910	869	862	851
Cl	949	901	858	848	837
OH	1000	972	793	777	770
SO_4	920	741	655	—	—
CO_3	—	—	—	638	631

[1] *Pogg.* **100**, p. 394; **105**, p. 360; **108**, p. 115; **111**, p. 60; **114**, p. 41; **120**, p. 493.

[2] *Rec. Trav. Néerland*, **7**, p. 269; and *Zeitschr. f. physikal. Chemie*, **3**, p. 423 [1888].

[3] *Wied. Ann.* **29**, p. 105 [1886].

0·7 Normal Solutions.

	H	NH_4	Li	K	Na
I	—	954	940	932	924
NO_3	981	954	934	930	922
Br	981	953	934	930	923
Cl	974	945	928	919	917
OH	1000	992	895	884	881
SO_4	970	853	813	804	803
CO_3	—	—	—	798	797

Röntgen and Schneider draw the following conclusions from this table.

'The substitution of one constituent of the compound in solution by another, e.g. I by NO_3, Br, Cl, OH, SO_4, or CO_3, alters the compressibility of the solution to an extent which is only slightly dependent on the nature of the other constituent of the compound (H, NH_4, Li, K, Na). It appears, then, as if each constituent of a chemical compound [1] exerted a specific effect on the compressibility of the solution of that compound, which effect is only slightly modified by replacing the other constituents by different substances; or, in other words, it seems as if the components of the dissolved body, and not the compound in which these components are contained, had the greatest influence on the compressibility of the solution.'

Water and ammonia are exceptions. The authors work out the possible causes of this: it is sufficient for us to notice that the constitution of each of the exceptional solutions is shown to be different from that of the other solutions examined by the fact that the two solutions in question are the only ones which are very bad conductors of electricity.

A research of Schumann [2] into the compressibilities of aqueous solutions of chlorides does not add to the results of Röntgen and Schneider. Schumann found that fairly constant products were obtained by multiplying the differences between the compressibilities of salt-solutions of specified contents (e.g. 10 per cent.) and that of pure water by the equivalents of the salts; the products sometimes, however, differed by as much as 20 per cent. This seemed to show that the effects of the metallic constituents of the

[1] This statement does not hold good for chemical compounds in general, but only for salts.

[2] *Wied. Ann.* **31**, p. 14 [1887].

chlorides examined by Schumann had nearly equal values in equivalent solutions; the method of representation adopted by Röntgen and Schneider is, however, much more in accordance with the facts.

8. **Freezing-points of salt-solutions.**—Observations show that the freezing-points of salt-solutions do not follow the simple laws which express the facts regarding the freezing-points of solutions of indifferent substances. The depressions of the freezing-points of salt-solutions are greater than the depressions which correspond with the molecular weights of the salts.

To bring these deviations within the scope of the expression $pv = RT$, which holds for solutions of indifferent substances, van 't Hoff added a coefficient i, and wrote the equation for salt-solutions as $pv = iRT$. The values of i were found to be always greater than unity. The values were approximately equal for similar salts; this follows immediately from the fact, enunciated by de Coppet, that the molecular depressions of freezing-point are equal for solutions of similar salts. The quantity i, which was at first regarded by van 't Hoff as a constant, was found to depend on concentration, in the way that i regularly decreased as concentration increased. This changeability is very small for salts of the type of potassium chloride, it is more marked for salts of the type of barium chloride, and it reaches a maximum for salts which consist of polyvalent positive and negative ions.

If attention is confined to solutions of medium concentration, the depressions of the freezing-points of salt-solutions may be regarded, as was shown by Raoult, as an additive property. Raoult[1] gives the following rules. The molecular depression, calculated for one gram-molecular weight of salt in 100 grams of water, is the sum of the following constants :—

Monovalent negative radicles	(Cl, OH, NO_3, &c)	19
Divalent „	„ (SO_4, CrO_4, &c.)	9
Monovalent positive „	(K, H, NH_4, &c.)	16
Di- or poly-valent „	(Ba, Mg, Al, &c.)	8

[1] *Ann. Chim. Phys.* (6) **8**, p. 321 [1886].

The molecular depression for $BaCl_2$, e.g., is $8 + (2 \times 19) = 46$; for $AlCl_3$ it is $8 + (3 \times 19) = 65$.

Although Raoult's method of calculation can lead only to approximate values for the molecular depressions of salt-solutions of mean concentration, because of the changeability of the quantity i, nevertheless the applicability of this method shows that this property of salts is the sum of the properties of their ions and is conditioned by the nature of the compound only in a secondary way.

The dependence of i on the concentration is apparent from the following numbers, which are given by Arrhenius [1]:—

c	t	i	c	t	i
Sodium Chloride.			Lithium Chloride.		
0·117	0·424°	1·93	0·099	0·363°	1·94
0·194	0·687	1·87	0·165	0·606	1·94
0·324	1·135	1·86	0·275	1·019	1·95
0·539	1·894	1·85	0·458	1·729	2·00
Silver Nitrate.			Potassium Sulphate.		
0·056	0·214	1·86	0·036	0·184	2·68
0·140	0·501	1·81	0·091	0·405	2·35
0·341	1·143	1·73	0·227	0·950	2·21
			0·455	1·755	2·04
Sodium Sulphate.			Strontium Chloride.		
0·0280	0·141	2·66	0·043	0·231	2·84
0·0701	0·326	2·46	0·107	0·523	2·59
0·117	0·515	2·33	0·214	1·053	2·60
0·195	0·817	2·21	0·356	1·791	2·66
Cadmium Iodide.			Cadmium Sulphate.		
0·0544	0·161	1·57	0·042	0·108	1·37
0·136	0·320	1·24	0·104	0·237	1·21
			0·196	0·420	1·14
0·342	0·715	1·11	0·489	0·938	1·02
0·684	1·523	1·16	0·815	1·535	0·99
			1·36	2·68	1·04
Sulphurous Acid.			Oxalic Acid.		
0·091	0·259	1·51	0·069	0·211	1·62
0·159	0·410	1·36	0·131	0·375	1·51
0·279	0·690	1·31			
0·466	1·16	1·32	0·247	0·650	1·40
0·820	2·01	1·30			

[1] *Zeitschr. f. physikal. Chemie*, 2, p. 496 [1888].

The setting-forth of the laws which express the dependence of the changes in the values of i on the concentration does not concern us here.

9. **Vapour-pressures of solutions of salts.**—The earliest knowledge of the regularities which hold with regard to the vapour-pressures of solutions was gained by the study of aqueous solutions of salts, and these solutions still form the best known part of the subject. It is, therefore, sufficient to refer to the exposition in Chapter VII.; the relations which exist may be traced from the tables on pp. 191–193.

The comparison of the results is made difficult by the circumstance that the proportion between the depression of vapour-pressure and the contents of the solution is by no means constant, but sometimes increases and sometimes decreases as concentration increases. By comparing the measurements of solutions having the smallest contents, $n = \cdot 5$, the following results are obtained.

Salts of the type M′ R′, where M′ is a monovalent metal and R′ is a monovalent negative ion, in half-normal solutions, show a depression of vapour-pressure of 10·5 to 12·5 mm. This gives a value for n equal to from ·77 to ·91, in place of ·5, by using the formula $\frac{p - p'}{p} = \frac{n}{N}$, and putting $p - p' = 10{\cdot}5$ to $12{\cdot}5$, and $p = 760$, the number of molecules of water in a litre being $N = \frac{1000}{18} = 55{\cdot}6$. The value of i in van 't Hoff's formula, $p\,v = i\,R\,T$, amounts, in these cases, to from 1·54 to 1·82. If the substances were completely dissociated, i must be equal to 2, and the depression of vapour-pressure must amount to 13·7 mm. The values for the hydrochlorides of the amines, especially for tri-ethylamine hydrochloride, are remarkably small. It is probable that this is to be attributed to the vaporisation of a small quantity of the amine, whereby the vapour-pressure is raised, and, therefore, the depression is made to appear too small. The hydroxides of lithium and potassium form exceptions in the opposite direction; the values

of i in these cases are greater than 2. This is the more remarkable as sodium hydroxide shows a normal behaviour.

The compounds of the type $M'_2 R''$ behave somewhat irregularly. As one molecule can separate into three ions, the maximum depression of vapour-pressure for $\frac{1}{2}$ normal solutions is 20·5 mm. The numbers actually observed vary for the most part from 13 to 15, which correspond with values for i from 2 to 2·2.

Compounds of the type $M'' R'_2$ show much greater regularities. The depressions vary between 15 and 17 mm.; the corresponding values of i are 2·2 to 2·5. Individual exceptions are noticeable; e.g. the depressions of the vapour-pressures of solutions of the halogen compounds of mercury and cadmium are very small. It will be shown later [1] that the other properties of these solutions indicate a very small amount of dissociation of the dissolved salts.

The salts of the type $M'' R''$ depress the vapour-pressure of water to a remarkably small extent. We find here several values less than 6·8 mm., which is the number that corresponds with the condition of no dissociation.

A much better insight into these relations would have been obtained had a number of more dilute solutions been examined first of all. For the osmotic pressure at 100° in a half normal solution, to which the comparisons must be confined, amounts to at least 15 atmospheres, and rises to 30 or 40 atmospheres when the substance in solution is dissociated. It is not to be wondered at that considerable deviations from the simple law became apparent under the circumstances.

10. **Colours of salt-solutions.**—The colour of solutions is a property which is generally altogether constitutive, but for solutions of salts this property is additive. This result might be expected from the considerations which led to the supposition that the ions of a salt in solution exist independently one of the other; the fulfilment of this expectation is, in turn, a very strong proof of the accuracy of the supposition.

[1] In another part of the *Lehrbuch*.—*Translator*.

The colours of salt-solutions are essentially the colours of the parts of molecules, or ions, contained therein, and all salt-solutions which contain a certain ion must exhibit the characteristic colour of that ion. Should the expected colour not appear, we may conclude that the corresponding ion is absent.

The red colour of dilute solutions of cobalt salts, for instance, indicates the presence of cobalt-ions. The sulphate, nitrate, chloride, &c., have the same colour in solution; the colour is independent of the nature of the negative ions. If one of these solutions is boiled with an excess of potassium cyanide, it is decolorised, *and the colourless solution no longer shows the reactions of cobalt.* The compound potassium cobalticyanide, $K_3Co(CN)_6$ has been formed; the ions of this compound are 3K and $Co(CN)_6$; free cobalt-ions are no longer present. The green colour of a solution of a nickel salt is changed, under the same conditions, to yellow, which shows that the nickel-ions have entered into combination.

If the foregoing statement is correct, the intensity of the coloration of those salts whose ions are coloured must be proportional to the quantity of these ions, supposing that the part of the salt which is not separated into ions is itself colourless. An experimental examination of this question would not present special difficulties, but it has not been carried out as yet.

Special relations are observed when the non-dissociated salt is itself coloured. For instance, anhydrous cupric chloride, or a solution of this salt in indifferent solvents (wherein it is not separated into ions), is coloured intensely yellowish brown. Therefore, a solution of this salt, which contains many free ions of Cu and Cl, but also a certain amount of undissociated molecules of $CuCl_2$, will show the colour which results from mixing the blue of the copper-ions with the yellow of copper chloride. Agreeably with this conclusion, it is found that very dilute solutions of copper chloride—which contain but little undissociated salt—are blue, like solutions of other copper salts; but the

more concentrated the solutions become, and therefore the greater becomes the number of the non-dissociated molecules, the more does the colour incline towards green. Addition of hydrochloric acid, or raising the temperature, acts in the same way as increasing the concentration; in both cases, the number of copper-ions decreases, and the number of the undecomposed molecules of copper chloride increases.

The colour-changes shown by the indicators which are employed in the volumetric estimations of acids and alkalis belong to the class of phenomena now under consideration. Two conditions must be fulfilled in order that a colouring matter shall exhibit such a change: it must have an acidic or basic character, and it must not be a strong acid or base. The difference of colour shown in acid and alkaline solutions indicates that the colour of one of the ions of the substance is different from that of the non-dissociated substance.

Para-nitrophenol is an example of an indicator of acidic character. This compound is colourless when solid, or when dissolved in alcohol, in which solution no dissociation takes place. An aqueous solution, which contains a small number of negative ions $C_6H_4.NO_2.O$, is somewhat coloured; but when addition of an alkali, e.g. soda, causes formation of the salt $C_6H_4.NO_2.ONa$, which salt separates almost wholly into its ions, the intensely yellow colour of the ion $C_6H_4.NO_2.O$ comes suddenly into view, and enables the change from the acidic to the neutral or alkaline reaction of the solution to be distinguished very sharply.

The behaviour of the basic indicators, e.g. cyanin, is quite similar to that of the acidic indicators. A solution of the free base, which is but slightly dissociated therein, has the blue colour of the undecomposed compound; when addition of an acid changes the base into a salt, the free ion of the salt is colourless.

These examples show that sometimes it is the free ion, and sometimes it is the undecomposed compound, which is coloured. This depends upon the fact that the absorption in either case takes place in the region of the invisible rays. The absorption often remains in the visible spectrum, and

only changes its position; this occurs with all indicators which do not change from a colourless to a coloured state, but only show a change of colour, e.g. litmus.

The second condition which must be fulfilled by an indicator, viz. that the substance must not be a very strong acid or base, depends on the fact that strong acids and bases are dissociated almost completely in solution. Permanganates, for instance, do not change colour whether their solutions are acidified or made alkaline. Permanganic acid is such a strong acid that a solution of it consists, practically, of the ions H and MnO_4. If this is changed into a salt, e.g. $KMnO_4$, a dilute aqueous solution of this salt consists, essentially, of the ions K and $Mn\,O_4$, and so there is no reason why a colour-change should take place.

Chromic acid, and the chromates or dichromates, furnish a somewhat more complicated case. Solutions of the chromates are clear yellow; solutions of the dichromates are red-yellow. Free chromic acid has the same colour, and shows exactly the same absorption-relations,[1] as the dichromates. The chromates must, therefore, contain an ion different from that of the dichromates, and of free chromic acid. The first part of this statement is self-evident; the ions of potassium chromate, for instance, are 2K and CrO_4, those of potassium dichromate 2K and Cr_2O_7. That a solution of chromium trioxide does not contain the ions 2H and CrO_4—if it did, the colour of the solution would be yellow—but the ion Cr_2O_7, as may be concluded from the colour, and that this solution is a solution of dichromic acid, $H_2Cr_2O_7$, was shown by me[2] from the behaviour of the solution in question towards the electric current and on freezing.

Finally it may be mentioned that all these considerations must hold good for the wave-lengths which lie outside of the visible spectrum, as well as for the visible rays. A confirmation of this is found in Soret's observation,[3] that

[1] Settegast, *Wied. Ann.* **7**, p. 242 [1879].
[2] *Zeitschr. f. physikal. Chemie*, **2**, p. 78 [1888].
[3] *Compt. rend.* **86**, p. 710 [1878].

nitric acid and the metallic nitrates show the same absorption-bands in the ultra-violet between the 16th and 18th cadmium-line, while the ethereal salts of nitric acid do not show these bands. This indicates that the bands in question belong to the ion NO_3; the nitric esters contain the same atomic group as the free acid and the metallic nitrates, but that they do not contain this group as a free ion is shown by the circumstance that none of these esters is a conductor of electricity. They cannot, therefore, show the absorption which is characteristic of the ion NO_3.

11. **Refraction-coefficients of salt-solutions.**—Gladstone found that the difference between the refraction-equivalents of the salts of two different metals with the same acid, in aqueous solution, remains the same, whatever is the acid in combination with the metals. By refraction-equivalent is to be understood the quantity $\frac{n-1}{d}m$, where n is the refraction-coefficient, d the specific gravity, and m the molecular weight, of the compound. The refraction-equivalent of the dissolved salt is obtained by deducting from the refraction-equivalent of a solution of the form $s + p\,H_2O$ —where s signifies one molecule of the salt—the value which corresponds with $p\,H_2O$. A number of refraction-equivalents thus determined are given in the following table:—

	Potassium	Sodium	Hydrogen	Diff. K-Na	Diff. K-H
Chloride	18·44	15·11	14·44	3·3	4·0
Bromide	25·34	21·70	20·63	3·6	4·7
Iodide	35·33	31·59	31·17	3·7	4·2
Cyanide	17·12	—	—	—	—
Sulphocyanide	33 40	—	—	—	—
Nitrate	21·80	18·66	17·24	3·1	4·5
Metaphosphate	—	19·48	18·68	—	—
Hydrate	12·82	9·21	5·95	3·6	6·8
Alcoholate	27·68	24·28	20·89	3·4	6·8
Formate	19·93	16·03	13·40	3·9	6·5
Acetate	27·65	24·05	21·20	3·6	6·5
Tartrate	57·60	50·39	45·18	3·6	6·2
Carbonate	34·93	28·55	—	$2 \times 3{\cdot}2$	—
Sulphate	30·55	—	22·45	—	$2 \times 4{\cdot}1$
Dichromate	79·9	72·9	—	$2 \times 3{\cdot}5$	—
Hypophosphite	25·94	20·93	—	$2 \times 3{\cdot}0$	—

The table shows that all the sodium salts, e.g., have a molecular refraction less by 3·4, in round numbers, than the corresponding salts of potassium. The difference between the molecular refractions of the salts which have different negative constituents is also independent of the metallic constituent; the iodides, e.g., show values which are very nearly 10 units greater than those of the corresponding bromides.

The occurrence of constant differences between the values of specified properties of a series of similar substances, which show equal differences of composition, is a proof that these properties must be looked on as additive, i.e. as the sums of two values which are independent of one another, and each of which belongs to one of the two constituents. The molecular refractions of salts belong to this category.

The foregoing table also shows that the rule ceases to be universally applicable when the acids are brought into the comparison. The strong mineral acids, which show a difference compared with their potassium salts of about 4·4, vary much from the weak organic acids, for which the difference is much larger, the mean being about 6·6. These variations are very closely related to the deviations from the simple laws of solutions which are exhibited by the substances in question. The deviations of the salts and strong acids are comparable, as both show large deviations and both give values for i which approach the number 2. In opposition to this, the weak acids show normal values for i. The first substances are largely dissociated, the latter are only slightly dissociated; in the first cases the refraction-values of dissociated ions are compared, and in the latter cases the values of the dissociated potassium-ions are compared with those of the undissociated hydrogen. It follows from the variations between the two differences that the refraction-equivalent of hydrogen (calculated by the n-formula) is increased by about 2·2 units by the change from the state of combination to that of dissociation.

These relations become very apparent in the measure-

ments made by M. Le Blanc [1] of the chlorinated acetic acids and their sodium salts. The following numbers were obtained :—

	Acid	Sodium Salt	Diff.
Acetic acid	21·4	24·5	3·1
Monochloracetic acid . .	29·7	32·8	3·1
Dichloracetic ,, . .	38·7	41·4	2·7
Trichloracetic ,, . .	47·7	49·6	1·9
Hydrochloric ,, . .	14·5	15·8	1·3

While acetic acid and monochloracetic acid, which are only slightly dissociated in aqueous solutions, show equal differences as against their sodium salts, the differences become gradually less for the other acids, the dissociation of which gradually increases, until they reach a minimum for hydrochloric acid as compared with sodium chloride. The difference 1·3 is smaller than that found by Gladstone, which was 2·2 ; but it is to be noted that the measurements of Le Blanc were made for the sodium line, while Gladstone's determinations were calculated for the line A of the solar spectrum.

12. **Magnetic rotations of salts.**—The extent to which organic compounds rotate the plane of polarisation of a ray of light under the magnetic influence is closely related to the refraction-powers of these compounds ; and a similar connexion between these phenomena is shown by salts and their solutions, but in a more marked way.

In the first place, the specific magnetic rotation of a solid salt is different from that of a solution of the same salt. Becquerel found the specific rotation of solid sodium chloride to be 1·21, and that of a solution of this salt to be 1·57, which is almost 30 per cent. greater than the value for the solid salt, the value for carbon disulphide being taken as unity. The conclusion follows that the ions, Na and Cl, possess a greater magnetic rotation than the compound NaCl.

[1] *Zeitschr. f. physikal. Chemie*, **4**, p. 553 [1889].

The rotation of a mixture of different substances is made up of the values belonging to the several constituents, proportionally to the quantity of each. Perkin found that this statement held good also for aqueous solutions of indifferent substances. Perkin[1] examined formic acid, acetic acid, propionic acid, and alcohol. The molecular rotation in each case was so nearly equal to the sum of the rotations of the organic substance and water, that the supposition of the formation of a compound of these two was untenable. The comparison of the rotation of propionic acid + water, $C_3H_6O_2 + H_2O = C_3H_8O_3$, with that of glycerin, $C_3H_8O_3$, is instructive; the empirical composition is the same; the rotation in the first case is 4·512, and in the second case 4·111.

In a second communication, Perkin[2] examined the question whether chloral hydrate contains water as such, or is trichlorethylidene glycol, $CCl_3CH(OH)_2$. The numbers were:—

	Mol. rotation
Chloral	6·590
Chloral hydrate	7·037

As the difference is only ·447, in place of 1, which is the value for the rotation of H_2O, the conclusion was drawn that chloral hydrate is trichlorethylidene glycol. The results obtained with acetic aldehyde were more complicated; the measurements indicated that a partial combination of water occurred, but this combination required a considerable time before it was accomplished.

The results with sulphuric acid were different. The molecular rotation of this compound was found to be 2·315; as the rotation of methyl sulphate was 4·013, each methyl group increased the rotation by ·849. Other acids gave values very similar to that of sulphuric acid, so that the behaviour of this acid was normal. After adding water to sulphuric acid the following results were obtained:—

[1] *Journ. Chem. Soc. Trans.* 1886, p. 777. [2] *Ibid.* 1887, p. 808.

	Mol. rotation	Difference
H_2SO_4	2·315	—
$H_2SO_4 + H_2O$	3·188	·873
$H_2SO_4 + 2H_2O$	4·113	·925
$H_2SO_4 + 3H_2O$	5·064	·951

The behaviour in this case differed from that observed with other compounds; the addition of the first molecule of water increased the rotation by ·873, while the increase for the second and for the third molecule approached the normal value. These results suggested the formation of a compound of the acid with water; Perkin supposed that this occurred, although this supposition was opposed to certain facts.

Nitric acid behaved somewhat differently.[1] The rotation of the pure acid was 1·18, and that of the aqueous solution $HNO_3 + 2·67\ H_2O$ was 3·656; the difference gives 2·476 for the rotation of the water, instead of 2·67. A decrease, therefore, occurred, but it was less than that noticed in the case of sulphuric acid. The differences between the rotations of nitric acid and its ethereal salts were found to be quite the same as those between organic acids and their esters.

Assuming that the results for sulphuric and nitric acid indicate the formation of hydrates of these acids, a similar conclusion cannot be drawn from the results for the halogen acids. The observed results led to the following magnetic rotations: HCl = 2·187, HBr = 4·016, HI = 8·211. Aqueous solutions of these acids gave as follows:—

HCl		HBr		HI	
Per cent.	Mol. rotation	Per cent.	Mol. rotation	Per cent.	Mol. rotation
41·7	4·045	65·6	7·669	67·0	17·769
36·5	4·215	56·6	8·061	65·1	17·868
30·9	4·303	39·7	8·415	62·0	18·117
25·6	4·405	24·6	8·547	56·8	18·308
15·6	4·419	15·5	8·519	42·7	18·403
				31·8	18·451
				20·8	18·428

[1] *Journ. Chem. Soc. Trans.* 1889, p. 680.

The numbers under *per cent.* give the percentages of haloid acid in the solutions; those under *mol. rotation* give the calculated rotations of the haloid acids.

Instead of decreasing, as was the case with the oxyacids examined, the molecular rotations of these acids showed very considerable increases on addition of water; the increase amounted to about 10 units in the case of HI. Moreover the numbers did not remain constant, but increased regularly as the quantity of water increased. The fact that the values observed for a solution of hydrochloric acid in isoamylic ether were 2·211 and 2·265, in place of the calculated number 2·187, showed that the numbers in the above table were not to be ascribed to an erroneous method of calculation.

These facts show that water exerts a special effect on the acids in question, and that this effect cannot be looked on as consisting in a combination of the water with the acids. It is only the strong mineral acids which experience this effect; the weak organic acids show no trace of it.

The results described in the preceding paragraphs lead us to seek for the cause of the phenomena in the dissociation of the strong mineral acids into their ions, in aqueous solutions. The measurements made by Perkin of the rotation of hydrochloric acid in isoamylic ether and in water, respectively, confirm this conclusion. The agreement between the values observed for the solution in isoamylic oxide, and the value calculated for HCl, points to the non-dissociation of hydrochloric acid in this solvent; this is confirmed by the fact that this solution does not conduct electricity.

The molecular rotations of solutions of ammonium salts were found to vary very little with dilution. The observed numbers, taken as a whole, were distinctly greater than those calculated from the sums of the rotations of the constituents, and the differences were nearly the same as those in the cases of aqueous solutions of the free acids. For instance :—

	Observed	Calculated	Diff.	Diff. for the acids
NH_4Cl	6·10	4·30	1·80	2·22
NH_4Br	10·18	6·13	4·05	4·52
NH_4I	20·00	10·33	9·67	10·22

Similar results were obtained for the salts of the substituted ammonias.

From these results Perkin concluded that the acids and bases in the solutions in question existed uncombined with one another. This conclusion is evidently inadmissible. For the solutions have neither the smell nor any other property of the free bases or acids, and the heat which is produced when these are brought together shows that some reaction, at any rate, has occurred between the acids and the bases. It is much better to interpret the observed behaviour as indicating that the solutions of ammonium salts contain ammonium and halogen in a state of dissociation, and those of the halogen acids contain hydrogen and halogen, and that in both cases the molecular rotations of the dissociated halogens come into play.

This supposition receives marked support from a series of observations made by Perkin, but interpreted wrongly by him. The rotation of sulphuric acid is decreased by solution in water, i.e. by separation into its ions; the decrease amounts to ·3 in concentrated solutions of the composition $H_2SO_4 + 3\,H_2O$, and probably to about 1·0 in dilute solutions. The calculated rotation of ammonium sulphate is 5·96; this is obtained by adding the rotation of pure sulphuric acid, 2·32, to twice the rotation of ammonia, $1·82 \times 2$; the observed rotation of ammonium sulphate is 4·98, which is ·98 less than the calculated value. This difference agrees with the difference between the rotations of non-dissociated [1] and dissociated sulphuric acid, and the

[1] Undiluted sulphuric acid is not dissociated, and it is not a conductor of electricity; the same holds for all other acids.

agreement is the more remarkable as the deviation is in the opposite direction in this case.

The results with nitric acid and ammonium nitrate are similar. Nitric acid, when as nearly as possible free from water, has the rotation 1·18; with 2·7 H_2O the rotation of the acid is ·99; in this case, also, the rotation of the ions is less than that of the undecomposed acid. In the same way the rotation of ammonium nitrate, 2·32, is less than the calculated, viz. 3·0. It may then be concluded that somewhat dilute solutions of nitric acid would give an extremely small molecular rotation for the acid, probably about equal to ·5.

Unfortunately Perkin has not yet examined the ammonium salts of weak acids. There can be no doubt that such salts as ammonium formate &c., when in aqueous solution, would show molecular rotations which would not be the sums of the rotations of the components of the salts. But the rotations must be the sums of those of the components if Perkin's view is correct. It would be easy, then, to make a crucial experiment which should decide between the two theories. Inasmuch as Perkin is almost the only chemist who is in a position to measure the values of magnetic rotations, it is much to be wished that he would carry out this simple investigation.

No extensive investigation has been made into the values of the magnetic rotations of other salt-solutions. From what has been done, the supposition may fairly be made that the property in question will be found to be an additive one, in the sense already explained. The determination of the constants for the different ions has an especial interest, inasmuch as relations will probably be found between these and the periodic arrangement of the elements.

13. **Optical rotatory powers of salt-solutions.**—The capability which certain liquid substances possess of rotating the plane of polarisation of light, depends upon an altogether special condition or constitution of these substances, and it

must therefore be looked upon as a constitutive property. The investigation of organic compounds which possess this property has not brought to light any trace of an additive character in the property in question. The power of rotating the plane of polarisation depends upon the presence in the molecule of the compound of a so-called asymmetric carbon atom, and the intensity of the rotation is connected, in a very complicated way, with the radicles which are in combination with this asymmetric carbon atom. The following values, for instance, have been obtained for the molecular rotatory powers of certain compounds:—

Methyl ester of diacetyltartaric acid . . .	−14·3°
Ethyl „ „ . . .	+1·0
Propyl „ „ . . .	+6·5
Isobutyl „ „ . . .	+10·3

The molecular rotations of aqueous salt-solutions stand in striking opposition to the foregoing statement. The compounds of strong bases with weak acids, and those of strong acids with weak bases, follow the simple law that *the molecular rotatory powers of these salts in somewhat dilute solutions are independent of the nature of the inactive parts of the salts.*

This statement was established by A. C. Oudemans,[1] who found especially that solutions of equal concentrations of salts of the mono-acid alkaloids have equal rotatory powers independently of the acids in combination with the alkaloids, and independently of whether the acids are present in excess or not. The salts of di-acid alkaloids showed certain variations, according to the strengths of the acids present; but these variations disappeared when the acids were present in excess.

Similar results held good for the strong acids. The rotations observed for the potassium, sodium, and ammonium salts of podocarpic acid were + 134°, 133°, and

[1] *Beiblätter*, 9, p. 365; from *Versl. R. Aka . Wet. Amsterdam* (3), 3, p. 408 [1885].

130°, respectively; the following values were found for the salts of quinic acid:—

K	Na	NH_4	Ba	Sr	Ca	Mg
48·6°	48·9°	47·9°	46·8°	48·7°	48·4°	47·9°

The statement was confirmed by measurements made by Hoppe-Seyler for the salts of cholic acid — K = 28°, Na = 29°—and by Landolt for the tartrates and camphorates. The camphorates gave K = 20°, Na = 21°, NH_4 = 20°; the acid tartrates gave Li = 28·5°, NH_4 = 28·5°, Na = 27·5°, K = 28·3°; the numbers observed for the neutral tartrates were Li_2 = 38·6°, $(NH_4)_2$ = 42·9°, Na_2 = 39·9°, K_2 = 43°, Mg = 41·2°, NH_4.Na = 41·2°, NH_4.K = 42·6°, Na.K = 41·6°, &c.

Schneider [1] gave the following numbers for the maximum dilutions of solutions of salts of malic acid:—

	K	Na	Li	NH_4
Acid salts	10·7°	11°	11·9°	10·3°
Neutral salts	15·4	17·5	18·6	15

More recent measurements made by W. Hartmann [2] for camphorates agreed even better than these. I give the numbers for maximum dilutions:—

	Li_2	Mg	$(NH_4)_2$	Ca	Na_2	K_2	Ba
Neutral salts . .	37·5°	39·5°	38·4°	39·1°	36°	36·1°	36·5°

When it is remembered what large differences are made in the optical rotatory powers of active substances by the smallest change in their molecular constitution—e.g. the substitution of hydrogen in tartaric acid by an alkyl radicle, or acetyl, raises the rotatory power enormously—the conclusion cannot be avoided, that the two constituents of a

[1] *Annalen*, **207**, p. 286 [1881]. [2] *Berichte*, **21**, p. 221 [1888].

salt exert a much smaller effect on one another, or that the reaction between them is much less, than in such organic compounds as esters, &c., which are otherwise similar to the salts.

The molecular rotations of the free acids differ very much from those of the salts. This is explained by the fact that the properties of solutions of most of the optically active acids show that these acids undergo dissociation only to a small extent. While the rotatory power of a solution of a neutral tartrate depends on the free ion $C_2H_2(OH)_2(CO_2)_2$, the rotatory power of a solution of free tartaric acid depends chiefly on the undecomposed acid $C_2H_2(OH)_2(CO_2H)_2$, and the rotation of this molecule is very different from that of the ion. But the number of free ions in the solution of the free acid increases as dilution increases; therefore, the molecular rotation of tartaric acid in aqueous solutions must approach that of the tartrates as the solution becomes more dilute. Arndtsen [1] measured the rotatory powers of solutions of tartaric acid; I have calculated the results to molecular rotations:—

Quantity of tartaric acid in 100 parts of the solution	$[m]_D$	Quantity of tartaric acid in 100 parts of the solution.	$[m]_D$
90	4·88°	40	14·66
80	6·84	30	16·60
70	8·79	20	18·56
60	10·74	10	20·52
50	12·70		

The molecular rotatory power of the tartrates is equal to about 42; so that a 10 per cent. solution of tartaric acid is still far removed from this value.

A similar state of matters holds good for the other acids and their salts. An optically active acid which is largely dissociated in the free state should show the same molecular rotation as its salts, when in somewhat dilute aqueous

[1] *Pogg.* **105**, p. 312 [1858].

solution. Compounds of this character have not been examined as yet. Such compounds will probably be easily found among the acid sulphuric esters of the optically active alcohols, such as amyl hydrogen sulphate.

There is another point concerning the solutions of tartaric acid which has hitherto been obscure, but which may now be explained. Concentrated solutions of 40 to 50 per cent. show an anomalous rotatory dispersion; they rotate the rays of mean wave-length—belonging to the green portion of the spectrum—to the greatest extent, and the rays of greater wave-length as well as those of smaller wave-length to a less extent. Biot,[1] who made this observation, was able to reproduce a similar phenomenon by mixing dextro-rotatory and lævo-rotatory liquids. It is not improbable that the anomaly is caused by the different active substances present in a solution of tartaric acid, viz. the unchanged acid and the free ions, which possess very different rotatory powers. This explanation is in keeping with the fact that the anomaly disappears in solutions of tartrates in which the number of free ions is so great as to overpower the influence of the small quantity of undecomposed salt.

14. Surface-tensions of salt-solutions.—Of all the properties of salt-solutions, the first to which an additive character was attributed was the surface-tension.[2] This was done at first, it is true, erroneously; for Valson[3] at a later time traced this back to the circumstance that the capillary ascents of equivalent solutions are inversely proportional to their specific gravities, so that the surface-tensions of these solutions must be equal. At a later time, Quincke[4] established the validity of a relation of this kind for a number of different chlorides, but this result was called in question by Volkmann.

Röntgen and Schneider[5] examined the surface-tensions

[1] *Ann. Chim. Phys.* (3) **56**, p. 405 [1852].
[2] Valson, *Ann. Chim. Phys.* (4) **20**, p. 361 [1870].
[3] *Compt. rend.* **74**, p. 103 [1872]. [4] *Pogg.* **160**, pp. 337, 560 [1877].
[5] *Wied. Ann.* **29**, p. 202 [1886].

of several salt-solutions with the object of finding stoïchiometrical relations. The following table contains the results, in terms of an arbitrary unit :—

—	H	Li	Na	K	NH_4
·7 Normal Solutions.					
I	—	112·3	112·6	112·5	112·3
NO_3	110·6	112·8	112·9	112·6	112·6
Br	110·9	112·9	113·0	112·8	112·9
Cl	111·1	113·2	113·2	113·2	113·1
OH	111·5	113·3	113·4	113·5	108·7
SO_4	111·6	114·2	114·1	114·1	114·0
CO_3	—	—	115·6	115·4	—
1·5 Normal Solutions.					
I	—	113·2	113·8	113·6	113·1
NO_3	109·8	114·2	114·3	113·9	113·9
Br	110·4	114·4	114·7	114·7	114·3
Cl	110·9	115·0	115·1	114·8	114·5
OH	111·5	115·2	115·9	115·5	106·8
SO_4	112·5	117·6	—	—	116·9
CO_3	—	—	117·5	118·2	—

These numbers approach each other nearly, but they are not quite identical. But the additive character of the property of surface-tension is very manifest; the order is almost always the same, both in the horizontal and the vertical series, and only the very small values of the corresponding differences make these appear less constant. Aqueous ammonia is the only exception ($NH_4.OH$); this compound seems not to come in the proper position in the series. But this compound is certainly much less dissociated than any of the others, so that its molecular condition is not comparable with that of the other solutions. This apparent exception is therefore a remarkable confirmation of the general relations which have been developed in the preceding paragraphs.

The surface-tension of an aqueous salt-solution may, then, be regarded as, on the whole, an additive property.

15. Other properties.—A comprehensive investigation of the viscosity of inorganic salts has been conducted recently

by J. Wagner.[1] The results show that the viscosity of dilute salt-solutions is essentially an additive property; this conclusion had been arrived at by Hannay,[2] from results which were inadequate, and in some cases erroneous. The conclusion is only a first approximation; this is shown by the following values for the viscosity-constants of various salts, determined with half-normal solutions, and referred to *equivalent* quantities of the salt.

	Sulphate	Nitrate	Chloride
Aluminium	1·378	—	—
Barium	—	1·042	1·115
Beryllium	1·351	—	—
Lead	—	1·077	—
Calcium	—	1·117	1·155
Cadmium	1·337	1·157	1·136
Potassium	1·090	0·956	0·967
Cobalt	1·349	1·149	1·206
Copper	1·349	1·166	1·209
Lithium	1·291	—	1·130
Magnesium	1·344	1·170	1·192
Manganese	1·351	1·184	1·206
Sodium	1·221	1·052	1·099
Nickel	1·350	1·175	1·196
Silver	—	1·045	—
Strontium	—	1·100	1·137
Zinc	1·355	1·170	1·209

The difference between sulphates and nitrates is fairly constant, amounting to from 130 to 150. Nitrates and chlorides approach one another; the latter generally have values about 30 to 50 greater than the former. The differences between the salts of two metals generally agree, at least in their sign. The value of the difference is approximately constant for nitrates and chlorides, but it is much larger for the sulphates. This depends on the influence which is exerted on the viscosity by the molecular condition of the salts, besides that exerted by their composition. It can be shown that the condition of solutions of chlorides is much more comparable with that of nitrates than of sulphates.

[1] *Zeitschr. f. physikal. Chemie*, **5**, p. 31 [1890].
[2] *Proc. R. S.* **28**, p. 279 [1879].

The differences which are observed when the viscosities of strong and weak acids are compared with those of their sodium salts are very similar to the differences which Gladstone observed when he compared the molecular refractions of such compounds. The following table makes this clear [1] :—

	Free acid	Na salt	Diff.
Hydrochloric acid	1·070	1·099	29
Hydrobromic „	1·038	1·062	24
Chloric „	1·053	1·089	36
Nitric „	1·022	1·052	30
Perchloric „	1·002	1·035	33
Phosphoric „	1·285	1·476	191
Arsenic „	1·271	1·494	223
Formic „	1·036	1·197	161
Acetic „	1·127	1·400	273
Propionic „	1·210	1·528	318
Butyric „	1·279	1·670	391
Isobutyric „	1·281	1·699	418
Lactic „	1·261	1·493	232

It is evident that the acids which were examined fall into two well-characterised groups : the strong mineral acids, whose sodium salts have only slightly greater viscosities than the acids themselves ; and the weak mineral acids and organic acids, whose sodium salts have much greater viscosities than the acids.

Finally, the thermal capacity of salt-solutions is also an additive property. Marignac [2] examined this property with special reference to the existence of a constant difference for analogous salts, and he showed that this way of representing the results applied to about one half of the salts which were examined. The following considerations show why the whole of the salts did not come within the scheme.

While all the properties hitherto discussed refer to the existing condition of the solutions examined, the specific heat refers to the change of this condition. If we imagine

[1] R. Reyber, *Zeitschr. f. physikal. Chemie*, **2**, p. 744 [1888].
[2] *Ann. Chim. Phys.* (5) **8**, p. 410 [1876].

a completely dissociated solution, the condition of which remains the same when the temperature is changed, then the specific heat of this solution is dependent only on the nature and number of the ions, and it may be represented as the sum of the values for these ions. It is different when, as generally happens, only a part of the salt is dissociated. A change of temperature now causes a change in the amount of dissociation, and heat is used or produced. These thermal changes are altogether of a constitutive character, and are dependent on the special condition of the substance; inasmuch as they form a part of the total value of the specific heat, the additive character of this is effaced.

This way of looking at the matter shows, incidentally, that the numerical values of the specific or molecular heats are specially suited for the examination of the processes which are indicated above.

16. **Conclusion.**—A general survey of the considerations brought together in this chapter shows that *the properties of salt-solutions, taken as a whole, are of an additive character.* Arrhenius was the first to show that the theoretical significance of this general law lies in recognising that this independence of the properties of the ions, which are the constituents of the salts, points to a corresponding independence of the chemical relations of these ions. The appearance of these additive properties leads, therefore, to the same conclusion as was pointed to by the deviations from the colligative character of the properties of solutions in general shown by salt-solutions, and shown especially in their osmotic pressures and the conditions of their freezing and evaporation, and serves as an additional support to this conclusion.

On the other hand, the universality of the additive character of the properties of salt-solutions may serve as a guide in the study of other properties of salt-solutions which have not been examined hitherto. All the properties which have an additive or constitutive character when they belong

to indifferent substances may be expected to be additive in their nature when they belong to salt-solutions; and all properties which are colligative in the cases of non-electrolytic solutions will show regular deviations, corresponding with van't Hoff's factor i, in the cases of salt-solutions. The general characters of the laws which shall express properties of salt-solutions that have not been examined as yet may be predicted by applying these statements.

CHAPTER X

SIMULTANEOUS ACTION OF SEVERAL SOLVENTS

1. Division of a substance between two immiscible solvents.—There is a well-known and much-used laboratory-experiment, wherein a substance is removed from solution by shaking the solution with another liquid which does not mix with the original solvent, but withdraws the dissolved substance. Alkaloids are removed from aqueous solutions in this way by shaking with chloroform, and iodine or bromine by shaking with carbon disulphide. The fact that the operation must be repeated in order to remove the substance completely shows that the process is not one of absolute, but only of partial, separation : the laws of such cases have been worked out by Berthelot and Jungfleisch.[1]

When a specified solution, e.g. succinic acid in water, is shaken for some time with a liquid which is not miscible with the solution, e.g. ether, the dissolved substance divides itself between the two solvents so that the contents of one solution bear a definite proportion to the contents of the other. Berthelot and Jungfleisch apply the term *partition-coefficient* to the proportion between the quantities dissolved in equal volumes of the two liquids.

The following table illustrates this statement :—

Water	Ether	Quantity in solution in		Partition-coefficient
		Water	Ether	
70 c.c.	30 c.c.	42·4	7·1	6·0
49 „	49 „	43·8	7·4	6·0
28 „	55·5 „	47·4	7·9	6·0

[1] *Ann. Chim. Phys.* (4) **26**, p. 396 [1872].

The numbers which give the contents of the solutions represent c.c. of baryta water required to neutralise 100 c.c. of each solution.

The partition-coefficient depends on the temperature and the dilution. In the case of succinic acid, water, and ether, it becomes smaller as temperature decreases and dilution increases; the latter part of this statement is illustrated by the following numbers, which give the grams of succinic acid per 100 c.c. = p (temp. = 15°) :—

Water	Ether	Partition-coefficient
p = ·486	·073	6·6
·420	·067	6·3
·365	·061	6·0
·236	·041	5·7
·121	·022	5·4
·070	·013	5·2
·024	·0046	5·2

The partition-coefficient may be represented approximately as $C = 5{\cdot}1 + 3\ p$; it approaches a limiting value equal to 5·1 for maximum dilution.

While benzoic acid shows a partition-coefficient which, like that of succinic acid, decreases with dilution, the relation is in the opposite direction in the cases of oxalic, malic, tartaric, and acetic acid. I give only the interpolation-formulæ :—

Benzoic acid . . . . . $C = 63 + 100\,p$
Oxalic „ . . . . . $C = 10{\cdot}5 - 3{\cdot}3\,p$
Malic „ . . . . . $C = 49 - 5{\cdot}6\,p$
Tartaric „ . . . . . $C = 133 - 8\,p$

The partition-coefficient of ammonia increases rapidly. Similar relations were established for iodine and bromine in carbon disulphide and water.

Berthelot sought in vain for a numerical connexion between the partition-coefficient and the relative solubility of the dissolved substance. He found that, generally, the solvent which dissolved the substance to the greater extent, also withdrew more of it from the solution; but the

numerical value of the two proportions did not agree. For instance, 10 c.c. carbon disulphide dissolved 1·85 gram iodine at 15°, and 10 c.c. water dissolved ·014 gram iodine; the ratio of the solubilities was therefore 1 : 132, while the partition-coefficient was 1 : 410. In the case of succinic acid, ether, and water, the two numbers were 10·4 and 6·8.

Berthelot himself raised the objection that the ratio of the solubilities was determined for ether free from water, and for water free from ether, while the partition-coefficient was referred to ether saturated with water, and to water saturated with ether. The experiment was therefore performed again, by shaking together ether, water, and excess of succinic acid, with the result that 10 c.c. of the ethereal solution was found to contain ·103 gram, and 10 c.c. of the watery liquid ·609 gram, of succinic acid. The ratio, 6·0, is smaller than 6·9, which is the value of the partition-coefficient calculated by the interpolation-formula; Berthelot therefore regarded a connexion between the two quantities as out of the question. Nevertheless, it is easy to see that the ratio of solubilities and the partition-coefficient must be identical for saturated solutions. For if it be supposed that the quantity of succinic acid added to a mixture of ether and water is exactly that which the mixture can dissolve, then, when the liquids have separated, each will be a saturated solution of succinic acid, and at the same time both solutions will be in equilibrium, for neither will be able to withdraw succinic acid from the other; the proportion between the contents of the solutions will therefore be that of the solubilities and also that of the partition.

Berthelot puts forward a further consideration designed to show the impossibility of deducing *à priori* the identity in question. The partition-coefficient of bromine between water and carbon disulphide has a finite value at each moment, while the solubility of bromine in carbon disulphide, and also the solubility-ratio in reference to water, is

unlimited. This anomaly disappears when the definition of the partition-coefficient, which is referred, for the sake of convenience, to equal volumes of the solutions, is replaced by the more rational method of referring this ratio to equal quantities of the solvents. If the partition-coefficient is taken to be the proportion between the quantities of the substance dissolved in equal quantities of the two solvents, then, for the case that the dissolved substance is soluble without limit in one of the solvents, the partition-coefficient for a saturated solution, i.e. for a solution containing an infinite quantity of the substance, will also be without limit.

Berthelot also noticed certain relations between the partition-coefficients and the chemical characters of the dissolved substances, but these relations rested on too few examples to make them of especial significance; moreover, they nearly agreed with those relations which hold good between chemical composition and solubility.

Finally, a statement which has many important applications was enunciated and established, viz. that *in dilute solutions containing several substances, the partition-coefficients are as they would be were each substance present by itself.*

2. **Deductions.**—Some noteworthy conclusions are arrived at by applying van 't Hoff's conception of the analogy between solutions and gases to the simultaneous solubility of substances in two immiscible solvents. If, for example, we shake a solution of succinic acid in ether, with water, the water behaves towards the solution as towards a gas. As in the case of gas-absorption, so here, a certain quantity of the dissolved substance is taken out, and the equilibrium which results is conditioned by exactly the same law as conditions the absorption of gases; the ratio of the concentrations in both parts of the heterogeneous system must be the same.

That this connexion is valid only within certain limits in the cases examined by Berthelot and Jungfleisch, depends

on the fact that the organic acids examined by them change their molecular state, in aqueous solutions, as dilution changes, so that the simple relation in question cannot hold good.

Let us suppose that a third liquid, C, is added to each of the two liquids A and B, that C is not miscible with either A or B, but that it can take up the dissolved substance. Then the liquid C must come into equilibrium with both of the solutions, and the three partition-coefficients, between A and B, A and C, and C and B, are no longer independent of one another. But when equilibrium is established between C and A on the one side, and between C and B on the other side, the concentration in A and in B must be such that these two solutions also are in equilibrium, as otherwise a perpetual motion would be possible. We may suppose the place of the third liquid to be taken by a space containing a gas. Hence it follows that the partition-coefficient of a gas dissolved in two immiscible liquids must be equal to the proportion of the absorption-coefficients of the gas in the two liquids.

A number of similar considerations may be developed in the direction indicated in the preceding sentences. But as no experimental investigations have been made in this domain as yet, I content myself with suggesting such investigations by the demonstration made above.

3. **Solution-pressures.**—The laws which hold good when one of the liquids is somewhat soluble in the other, are similar to those which are operative when the liquid evaporates. Just as a liquid continues to evaporate into an empty space until a certain pressure is established, which pressure corresponds with a certain concentration, so the equilibrium of one liquid in contact with another is attained at a certain concentration of the second liquid, which concentration is conditioned by a definite osmotic pressure. This osmotic pressure, which is altogether analogous to the vapour-pressure, has been called the *solution-pressure* by W. Nernst,[1] who was the first

[1] *Zeitschr. f. physikal. Chemie*, **4**, p. 150 [1889]; **6**, p. 16 [1890].

to apply the analogy in question to draw more far-reaching conclusions.

As the vapour-pressure of a volatile substance is decreased by the solution therein of another substance, in proportion to the number of molecules, so must the solubility of a liquid, A, in another liquid, B, be decreased by solution of another substance in A. If l be the solubility of A, i.e. the quantity of A in the unit-volume of B, and l' be the solubility when another substance is dissolved in A, then the equation

$$\frac{l - l'}{l'} = \frac{n}{N}$$

must hold good, where n = the number of molecules of the dissolved substance, and N = the number of molecules of the solvent. This conclusion has been verified by Nernst in the following way (*loc. cit.*).

In each experiment 5 c.c. of valeric acid were shaken with 10 c.c. of water; so much of each was dissolved as to produce a solution which was ·541 normal. Different substances were then dissolved in the valeric acid, with the result that the solubility decreased to an extent which was directly proportional to the quantity, and inversely proportional to the molecular weight, of the substance added. The numbers obtained are given in the following table:—

	x	l'	$\frac{l-l'}{l'} \cdot \frac{M}{x}$	M	Calculated
Benzene	·182	9·90	25·2	78	75
,,	·431	9·39	20·9	78	89
Chloroform	·150	10·17	24·2	119·5	118
Menthol	·246	10·11	23·6	156	161
Camphor	·160	10·18	27·9	152	132
,,	·970	9·81	29·7	152	123
Xylol	·376	9·76	20·9	106	122
Stearic acid	·165	10·34	23·4	284	291

The numbers under x are the quantities of the substances added to 5 c.c. of valeric acid; those under l' are the solubilities, i.e. the number of c.c. of decinormal potash solution

required to neutralise 2 c.c. of the solutions; the solubility of pure valeric acid in the same units was 10·48. The hypothesis requires that the value of $\frac{l-l'}{l'} \cdot \frac{M}{x}$, where M is the molecular weight of the dissolved substance, should remain constant. The value of this quantity is calculated as follows. We have at the outset

$$\frac{l-l'}{l'} = \frac{n}{N};$$

now $n = \frac{x}{M}$, and $N = \frac{4{\cdot}13}{102}$, where 4·13 is the weight of valeric acid remaining at the end of the experiment, and 102 is the molecular weight of this acid. By substituting these values in the equation, we have

$$\frac{l-l'}{l'} = \frac{x}{M} \cdot \frac{102}{4{\cdot}13} \text{ or } \frac{l-l'}{l'} \cdot \frac{M}{x} = 24{\cdot}5.$$

The quantity $\frac{l-l'}{l'} \cdot \frac{M}{x}$ must be constant and equal to 24·5; the corresponding column of experimental results shows that the values vary irregularly about the theoretical value.

The column last but one contains the actual molecular weights of the dissolved substances, and the last column gives the molecular weights calculated by the formula $M = 24{\cdot}5 \frac{l'x}{l-l'}$. Although considerable differences are apparent in individual cases, nevertheless the agreement is sufficient to establish the validity of the supposition upon which the method is based. As the calculated molecular weights are proportional to the difference $l - l'$, and this difference represents 1·1 c.c. in the most favourable cases, it is evident that a small error in the titration causes a percentage error at least ten times greater in the difference on which the calculation is based.

Nernst showed, in the same communication, that the same relation holds for ether and water, and also for phenol and water. We have here then another *colligative*

property, and, therefore, a new method for determining molecular weights.

4. **Further applications.**—The estimation of the quantity of the liquid A which has been dissolved may be determined by any quantitative process. As we deal in all cases with differences of solubility, it is evident that *differential methods* are most suitable.

A special instance of the differential method has been worked out by Nernst (*loc. cit.*), by using the freezing-point as a measure of the quantity of the substance in solution. If excess of ether is shaken with water, and the whole is cooled, the freezing of the ether saturated with water may be determined with great accuracy, as ether must separate along with the separating ice, because the solution was saturated and therefore the concentration cannot change. If a substance which is insoluble in water is added to the ether, the *solution-pressure* will be decreased in reference to the water, and therefore the freezing-point will be raised. The equation again holds good

$$\frac{t - t'}{t'} = \frac{n}{N}$$

where t is the freezing-point of water saturated with pure ether, and t' is the freezing-point of water saturated with the ethereal solution.

The equation, however, is not quite accurate. It would be accurate if the solubility of ether in water were independent of the temperature. But this is not the case, and, therefore, the temperature-difference $t - t'$ expresses not only the effect of the dissolved substance on the solubility of the ether in water, but also the effect of the changeable solubility of the ether. The necessary correction is obtained from the corresponding calculation of a cyclical process, and the corrected equation takes the form

$$\frac{t - t'}{t'} = \frac{n}{M}\left(1 - \frac{l}{s\lambda}\right)$$

where λ is the heat of fusion of water, l is the heat of

solution of ether, and s is the quantity of water which separates from the ether between the two temperatures. The individual numbers are given in Nernst's memoir. The following table contains some results obtained by this method:—

	x	$t-t'$	Corr.	M	Calculated
Benzene . . .	2·04	·078	·080	78	78
„ . . .	5·88	·208	·219	„	82
„ . . .	13·20	·445	·496	„	82
Naphthalene . .	3·42	·080	·082	128	128
„ . .	6·60	·149	·155	„	130
„ . .	10·50	·232	·246	„	131
Iodine	4·76	·060	·061	254	239
„	11·30	·120	·124	„	280

The numbers under $t - t'$ are the increases of the freezing-point produced by the addition of the quantities of the dissolved substances given under x, calculated for 100 grams of ether; the corresponding differences corrected by the equation already stated are given under the heading 'corr.' The actual molecular weights of the dissolved substances are given under 'calculated.' The agreement is satisfactory. The temperature-difference can be estimated very accurately, notwithstanding its small value, because no marked change of concentration occurs during the separation of the ice and therefore no change of temperature is produced.

Nernst obtained equally good results by the use of ethylic acetate and water.

Finally, Nernst remarks that the boiling-method of Beckmann (p. 180) may be applied when two liquids are employed simultaneously. But this modification of Beckmann's method can scarcely be of practical value.

5. **Separation of solutions.**—Some liquids which mix in all proportions at a specified temperature separate into two heterogeneous portions when the temperature is changed. In such cases, two solutions of the liquids are formed; one of the liquids predominates in one solution, and the other in the other solution. These phenomena are a necessary

consequence of the considerations regarding the mutual solubilities of liquids which have already been dealt with (p. 40).

The result of this separation is the formation of two saturated solutions. As the condition of saturation does not depend on the relative parts of the mixture, since the equilibrium of saturation is obviously not destroyed by removing arbitrary portions of either layer after separation of the two layers, it must be concluded that the composition of the original mixture has no influence on the composition of the two layers after separation, provided that

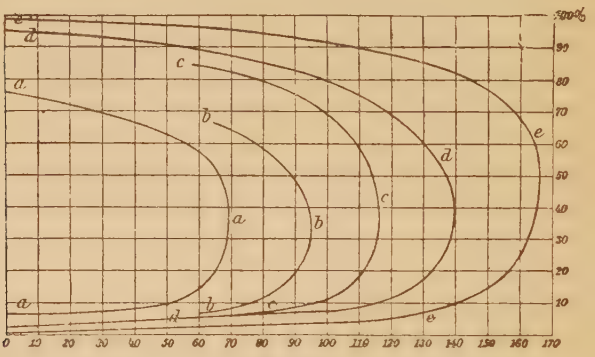


FIG. 35

enough of one substance is present, in proportion to the other, to ensure separation.

On the other hand, the temperature whereat the separation occurs is dependent on the proportion between the liquids in the mixture. This is shown in the behaviour of phenol towards water, which is represented in the curve *a a a*, of fig. 3, p. 42, which figure is reproduced here (fig. 35). Inasmuch as a liquid which contains less than 7 per cent. or more than 76 per cent. of phenol, remains, even at 0°, below the point of saturation of water with phenol, or that of phenol with water, such a liquid cannot be separated into two layers by cooling it to this temperature. But if the quantity of phenol is between 7 and 76 per cent., then, if solution has taken place at a higher temperature,

separation must occur at a lower temperature. The temperature whereat separation occurs will be the lower the nearer the percentage of phenol approaches one of the limits 7 and 76.

The more the mutual solubility of the liquids changes with changes of temperature the more will the composition of the separated layers also vary. This conclusion is not opposed to that which was arrived at already, to the effect that the composition of the layers must be invariable. For that conclusion has reference to a condition of equilibrium at a specified temperature, whereas we are now considering equilibrium at different temperatures. For instance, if a solution which has separated into two layers at 30°, is brought to 20° without agitating the liquid, the two layers have a different composition from those of a solution wherein separation begins only at 20°; the two layers of the first solution are no longer in solution-equilibrium at 20°. If the two layers of a liquid which separates at 30° are violently shaken together at 20°, the equilibrium belonging to this temperature is produced, and the two layers must now have the same composition as those of the solution wherein separation began at 20°.

This conclusion was confirmed, to some extent, by the experiments of Duclaux.[1] This investigator observed the influence of temperature, but he does not appear to have considered the method of avoiding this influence referred to above. Duclaux worked with mixtures of benzene and acetic acid; these were found to dissolve in all proportions at 15°, and the solution separated at lower temperatures into two layers which had the following compositions :—

Acetic acid	Benzene	Volume of the		Acetic acid in the	
		Upper layer	Under layer	Upper layer	Under layer
10 c.c.	15 c.c.	20·1 c.c.	4·9 c.c.	33·3	62·8
10 „	10 „	9·9 „	10·1 „	33·6	63·5
15 „	10 „	5 „	20 „	35·0	62·5

[1] *Ann. Chim. Phys.* (5) 7, p. 267 [1876].

The relative volumes of the layers changed at 1·20, nevertheless the composition of each layer remained almost unchanged; it would have remained quite unchanged had equilibrium of the solution been established at a constant temperature. An investigation in this direction is desirable, although the result may be foreseen with certainty.

6. **Ternary mixtures.**—While there are but few pairs of liquids which exhibit the passage from partial to complete mutual solubility, described in the preceding paragraph, at convenient temperatures, an unlimited number of ternary mixtures may be arranged to possess this property. The following is the general rule for finding such a grouping together of liquids:—

Let there be two liquids which dissolve one another only partially, then a homogeneous solution may always be produced by adding a third liquid which mixes in all proportions with each of the original pair.

The validity of this rule may be deduced from general considerations, as well as from experimental evidence, although no special investigation has been made to test the rule. It may also be said that the smaller the mutual solubility of the two liquids the greater is the quantity of the common solvent which is required to produce a homogeneous mixture.

As we are dealing with three substances the conditions of equilibrium are naturally more complicated. If we start with two immiscible liquids, A and B, and bring them into solution by addition of a common solvent, L, a separation into two layers will occur, in one direction or the other, by changing the temperature. Both layers will contain the three liquids; one will consist chiefly of A and L, with a smaller quantity of B, and the other will consist chiefly of B and L with a smaller quantity of A.

The phenomena which occur in mixtures of this kind have been very little studied as yet. The only investigator who has examined this subject, so far as I know, is

E. Duclaux.[1] The results of his investigations are as follows :—

When two liquids, e.g. amylic alcohol and water, are brought into solution by addition of a common solvent, e.g. ethylic alcohol, and separation into layers is caused by a change of temperature, the two portions consist of the immiscible liquids, A and B; the common solvent is able to divide itself between the two, and it is present, therefore, in nearly the same quantity in each layer.

If 15 c.c. amylic alcohol at 20° are mixed with 40 c.c. ethyl alcohol at 50° and 12·9 c.c. water, a clear solution is obtained which separates into two layers of 28 and 40 c.c. respectively, when the temperature is lowered by ·1°. A separation is also effected by adding a drop of water or a drop of amylic alcohol; the solution is sensitive to an excess of either liquid.

Duclaux analysed the two layers by finding the surface-tension of the liquid, by a drop-measurer, after having added water sufficient to bring the liquid to 5° äraometer strength. A preliminary experiment with synthetically prepared liquids had given the relation between the number of drops and the percentage of amylic alcohol. In this way he obtained the following table :—

Amyl alcohol	Ethyl alcohol	Water	Ratio of layers	Amyl alcohol		Ethyl alcohol	
				Upper	Under	Upper	Under
100	100	125	5·8	33 p. ct.	14·8 p.ct.	30·6 p. ct.	33 p. ct.
100	110	152	2·5	33·8	15·6	30·3	30·9
100	133	220	0·67	30·6	15·2	29	29·2
100	150	260	0·40	31·0	14·4	29	29
100	166	292	0·18	33·0	14·8	29	29
100	200	400	0·11	35·0	12·0	26	28

The composition of the liquids, after the third series, was made so that addition of a drop of water caused separation into layers. The mixture evidently behaved nearly in the same way as a binary mixture; the proportion between amylic alcohol and water (from the difference) remained

[1] *Ann. Chim. Phys.* (5) 2, p. 264 [1876].

nearly constant for all the mixtures, and almost the same quantity of ethylic alcohol was present in both layers. Similar results were obtained where the separation of the layers was effected by addition of a drop of amylic alcohol.

The following series of results was obtained by using acetic acid as the common solvent :—

Amyl alcohol	Acetic acid	Water	Ratio	Amyl alcohol		Acetic acid	
				Upper	Under	Upper	Under
100	66	95	4·3	40	14	25	26·9
100	100	174	0·61	38·2	15·8	25·2	26·8
100	140	288	0·12	41	14	26·0	26·8

The regulations noticed already hold good here also.

The mixtures described above separate into layers when they are cooled. There are others which become cloudy, and separate, when they are warmed. This happens with liquids which contain ether ; for instance, with a mixture of five volumes of alcohol at 86° with 10 volumes of ether and 6 of water ; or with a mixture of 10 c.c. of ether with 5 c.c. of acetic acid and 6·7 c.c. of water. In the last mixture, the acetic acid is found in nearly equal quantities in the two layers, thus :—

Ether	Acetic acid	Water	Ratio	Acetic acid	
				Upper	Under
100	36	50	1·9	19	19·6
100	40	60	1	19·5	20·5
100	44	72	0·65	20·5	20·4

The ratio of ether and water was not determined.

The relations are not always so simple. If a very small quantity of water is added to a solution of benzene and acetic acid, the solution becomes cloudy and separates into two layers, which are very similar in composition to those produced by lowering the temperature of the binary solution ; this is made clear by the following results :—

Benzene	Acetic acid	Water	Ratio	Acetic acid	
				Upper	Under
100 c.c.	50 c.c.	1·5 c.c.	42	31·2	68·6
100 „	66 „	1·8 „	5	35·9	60·9
100 „	100 „	2·0 „	1·25	35·6	63·1
100 „	150 „	2·7 „	0·28	30·8	68·5
100 „	250 „	3·3 „	0·05	32·5	71·9

The numbers under 'ratio' give the proportion of the volume of the upper to that of the under layer; the numbers in the two last columns, which give the quantities of acetic acid in the upper and under layers, show that these vary only slightly, but that the quantities in the two layers are not the same. We have evidently to do here with a limiting case in which the mutual solubilities of the liquids A and B—in this instance, water and benzene—are very small, and where, therefore, the power of the common solvent, acetic acid, to combine with each, is very different. For while the mutual solubility of acetic acid and benzene is unlimited only at temperatures above 15°, but is limited at lower temperatures, acetic acid and water mix with the greatest ease, and the mixing is attended with contraction and the production of much heat. In accordance with this, the portion of acetic acid in the water is greater than that in the benzene, and indeed it is very much greater in proportion to the quantity of water present.

7. **Influence of temperature.**—Duclaux used the mixtures described above as maximum and minimum thermoscopes. These mixtures are very sensitive towards changes of temperature: a change of temperature of less than ·1° generally suffices to cause cloudiness of the liquid and separation into two layers. The separation, when once it has been effected, remains if the temperature is restored to that at which a homogeneous solution would be formed. If the liquid is coloured with a substance which is soluble in water, this colouring matter passes almost completely into the lower layer and so makes the separation visible.

The compositions of the layers produced when equilibrium was established depend on the temperature, but the dependence is not very marked. Duclaux [1] found the following numbers for the mixture of water, amylic alcohol, and ethylic alcohol :—

Amyl alcohol	Ethyl alcohol	Water	Temp.	Ratio of layers	Amyl alcohol	
					Upper	Under
100	133	246	30°	0·44	29·3	16·1
100	133	219	20	0·67	30·6	15·2
100	133	191	10	1·2	31·3	14·2
100	133	164	0	1·5	31·6	13·5
100	133	133	−14	1·8	34·4	10·3

The quantities of water were arranged so that the separations took place at the temperatures given in the table. The ratios of the amyl alcohol in the two layers do not differ much.

8. **Applications.**—Duclaux did not consider the conditions which primarily determine the compositions of the layers. A survey of these conditions leads to the conclusion, which was arrived at by Konowaloff (p. 47), that two solutions in equilibrium must have the same vapour-pressure, and this must hold good for each constituent. The liquids must therefore separate in such a manner as to fulfil this condition. Now, all the vapour-pressures change in the same direction, with change of temperature, and in only slightly different proportions ; therefore, small differences of composition will correspond with considerable differences of temperature, as was found by Duclaux to be the case.

If the vapour-pressure of one portion is changed by the addition of some substance, the temperature whereat separation occurs will be considerably altered. If the substance added passes wholly into one of the layers, when separation is effected, certain general conclusions may be

[1] *Ann. Chim. Phys.* (5) 2, p. 275 [1876].

arrived at concerning the effect of the added substance. For instance, if a salt is added to the mixture of amylic alcohol, ethylic alcohol, and water, the salt will remain, practically, in the aqueous portion; the vapour-pressure of the water in this portion will be decreased thereby, and equilibrium will be established only by the passage of a corresponding quantity of water from the other layer into the first layer. Corresponding with this change in the proportion of the water there is quite another temperature whereat the liquid can become homogeneous, and the considerations put forward above show that this change of temperature must be relatively great.

This way of regarding the subject allows further conclusions to be drawn. The experiments of Duclaux seem to indicate that the change of the temperature of separation may be taken, as a first approximation, to be proportional to the change of composition, and this again may be taken as proportional to the relative change of vapour-pressure; hence, the temperature at which layers are formed is subject to the same laws as the vapour-pressure, so far as regards the addition of a salt.

We should, then, expect that the temperature-changes required to produce separation into layers would be proportional to the quantities of salt added, and would be equal for equimolecular solutions of similar salts. Some experiments, which I have caused to be carried out in this direction, have confirmed this expectation, so that, here again, we have a new method for determining molecular weights. This method has an advantage in that very small quantities of a salt cause very large changes in the temperature of separation; but the circumstance, that only in a few cases does the whole of the salt which is added remain in the aqueous layer, militates against the general application of this method: for if the salt passes into the other layer, the supposition on which the method is based is not fulfilled, and the regularities which were mentioned do not occur.

9. **Further considerations.**—The method used above of dealing with the equilibrium of two layers in contact may be adapted to every other process whereby one of the constituents of the mixture can be withdrawn. If such layers contain water, they must form ice at the same temperature, and the osmotic pressure of all the constituents present in both layers must have the same value. This circumstance affords important help in drawing conclusions, from experimental researches, regarding other properties of such mixtures.

Considerations of this kind enable us to express the conditions of equilibrium, but they do not give any insight into the mechanism of the processes. We must look for this in the surface of separation of the two immiscible liquids, and in the surface-tension which is present there.

An interior pressure of considerable magnitude prevails at the surface of every liquid, and, therefore, a certain amount of work must be done before a molecule can pass away from the liquid. If the liquid is surrounded by an empty space, this work attains its maximum value, and it is recognised in the form of heat of vaporisation. If, however, the first liquid, A, is surrounded by another liquid, B, then a molecule situated on the separating surface of A will experience an attraction into the second liquid, which attraction works in opposition to the interior pressure; the same thing will hold good for the molecules of B which are situated on the surface of separation. A process will thus take place analogous to the formation of vapour. The molecules which have the largest kinetic energy will leave the liquid A, as these are in a position to perform the necessary amount of work, and will enter the liquid B; and a similar process will take place with the liquid B in reference to A. If the amount of work which must be done to effect the interchange of molecules is very considerable, only a few molecules will be able to accomplish this work; the two liquids will be only partially soluble in one another.

Very varied relations may persist when the temperature is raised. As the number of molecules passing from one liquid into the other is a function of the interior pressure of both A and B, and is also a function of the mutual action of both liquids, it is possible for the function in question to be conditioned so that the mutual solubility of the liquids decreases, although the interior pressure of both liquids decreases with increasing temperature. Nevertheless, when the interior pressure becomes continuously less by the constant increase of the kinetic energy of the molecules accompanying the rise of temperature, the number of molecules passing from one liquid to the other—i.e. the solubility of one liquid in the other—must always finally increase. Hence, the two liquids must become more like one another, the amount of work required for the passage of molecules from one to the other must become less, and the surface-tension at the separating surface must decrease until it becomes equal to zero, where complete miscibility must result.

These processes are evidently very similar to the passage of a liquid into the state of vapour; the temperature of complete miscibility corresponds with the critical temperature.

The work which accompanies the passage of molecules from one liquid into the other changes its sign at temperatures above that of complete miscibility; at such temperatures work may be gained by the transference: for the energy gained by the mutual action of the heterogeneous liquids will overpower that used in the separation of the molecules of the same kind. Hence results the tendency to diffusion—the tendency, that is, of both liquids to occupy the largest space possible. In the cases of gases, the last condition alone is determinative, because the interior pressure of gases is very small. Boltzmann[1] has shown that work is gained by the mutual diffusion of two gases; if the addition of heat from outside is prevented, the system will be cooled by this process.

[1] *Sitzungsber. Wien. Akad.* **78**, p. 733 [1878].

Hence it follows that two thermal processes occur, of opposite signs, when two liquids are mixed. Heat is produced by the positive work which accompanies the mutual action of the heterogeneous molecules, and heat is used in the separation and spreading out of the homogeneous molecules; the sum of these may be positive or negative. The first part seems to be the greater in most cases, and hence two liquids usually become warmer when they are mixed. But cases are known where the opposite occurs, and, indeed, where the sign changes according to the proportion of the two parts (p. 38). The statements already made show that the explanation of this presents no difficulty.

If we have two liquids at such a temperature that they dissolve only partially, then the addition of a third liquid, which is miscible with both the others in all proportions, acts like a rise of temperature. The work which is required for the transference of the molecules will now be less, for a part of the work will be done in the reactions of the liquids with the common solvent, and this action, as has been explained, may allow an excess of work to remain. The two liquids, A and B, will dissolve more freely in one another, and, if enough of the third liquid is added, they will dissolve in all proportions.

Although there are no experimental data bearing on this point, yet it may be said with certainty that the surface-tension at the common surface of A and B must at the same time decrease gradually until it becomes equal to zero at the moment of complete miscibility.

10. Concluding remarks.—A general survey of the relations and laws of solutions which are presented in this book shows that these form one of the most important parts of physical chemistry.

The laws of solutions resemble the simple and important laws of gases, which were discovered about a century ago, and which have exerted a very great influence on the formation of chemical conceptions, in so far that many of the laws of solutions are *colligative* in their character—like

the law of Gay-Lussac concerning the volumes in which gases combine chemically—and they therefore lead to the same conclusions regarding the molecular constitution of matter as have followed from Gay-Lussac's law interpreted by the theory of Avogadro.

The extent of the domain included under solutions is, however, much larger than that dealt with under gases, and the relations observed in the former department are more complicated than those in the latter. Hence it happened that almost a century passed between the discoveries of the regularities which hold good in the two spheres, although these regularities are altogether similar.

The greater complexity of the subject of solutions makes advances in this department more difficult, but at the same time it gives greater importance to the results, for all those questions which could be answered formerly only from a knowledge of the substance concerned when in the gaseous state may now be answered from a study of the properties of a solution of the substance. While there are innumerable substances which are not known in the state of gases, there are but few which cannot be brought into solution. The silicates are almost the only widely distributed and very important substances which occur in nature that cannot be subjected to this method of investigation.

A knowledge of the laws of solutions is also most important inasmuch as almost all the chemical processes which occur in nature, whether in animal or vegetable organisms, or in the non-living surface of the earth, and also those processes which are carried out in the laboratory, take place between substances in solution. For instance, a sound judgment regarding physiological processes, or an explanation of the notable phenomena of resorption and secretion, is impossible without this knowledge; and the same statement holds for the greater number of the scientifically and technically important reactions. Looked at in this way, solutions are more important than gases; for the latter seldom react together at ordinary temperatures, whereas solutions

present the best conditions for the occurrence of chemical processes.

The discovery of the laws of solutions is full of significance for the advance of physical chemistry, for these laws are important helps in the investigation of the next problem, which is the laws of pure liquids. The colligative laws which hold good for gases and dilute solutions always maintain their character, because the molecules of gases and of dilute solutions are so far removed from one another, that neither the mutual actions nor the special natures, but only the numbers, of the molecules, come into play. But the individual characters of the molecules become of more importance when gases are compressed, or solutions are concentrated, and these, which appear at first as small deviations from the colligative laws, dominate more and more, until at last, in pure liquids, resulting from the continued compression of gases (below their critical temperatures), or from the disappearance of the solvent, they completely overpower the colligative laws.

The hope may be expressed that the possibility of representing and studying all these intermediate states, which can be accomplished easily and fully in the examination of solutions, will be of considerable help in making easier the study of the laws of pure liquids.

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